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LAND TREATMENT OF PETROLEUM REFINERY SLUDGES

by

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16. ABSTRACT

Petroleum API Separator sludge was applied to field plots to evaluate optimizatio of loading rates and frequencies for waste disposal by land treatment. Loading rates 3 to 13 weight percent and frequencies 1 to 12, respectively, per year were studied over an 18 month period. Total oil losses were proportional to the amount applied and averaged 54 percent over the study period. Saturates fraction loss was highest followed by aromatics, polars, and asphaltenes. Volatile losses were substantial at application, but relatively small over the long-term. Biodegradation of the oil followed first order kinetics with a rate coefficient of 0.003 day^{-1}. Heavy metals were immobile in the top 30 cm zone of incorporation. Facility design factors are discussed relating to field equipment operation, oil percolation prevention, runoff control, and proper tillings.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air, and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

The report contains technical information useful to those responsible for making decisions on operational aspects for oily residue waste disposal at land treatment facilities. Topics covered are (1) design criteria for loading rates, frequencies of applications, and tilling frequency, (2) fate of the waste's priority pollutants, and (3) atmospheric emissions assessment.

Clinton W Hall

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ABSTRACT

The purpose of this study was to identify, evaluate and optimize the factors which influence land treatment of oily residues. A research site owned by the University of Oklahoma was used. A total of 50, 6.1 m x 2.7 m (6 ft x 9 ft), plots were prepared and API Separator sludge was applied to the plots at loading rates between 3 and 13 weight percent per year, and loading frequencies from 1 to 12 times per year. The soil was analyzed for oil content, selected heavy metals, selected organic priority pollutants, pH, nitrate and chloride, over a 18 month period. Oxygen levels in the soil atmosphere, and the emission rate of volatile hydrocarbons were monitored. A laboratory study to identify and quantify volatile hydrocarbons emitted was also performed. Fractionation analysis of sludges and recovered oils were done for saturates, aromatics and polar compounds and asphaltenes.

Total oil losses were proportional to the amount of oil applied with mean losses over the study period equal to 54 percent of the oil applied. Losses of the saturates fraction were highest followed by aromatics, polar compounds, and asphaltenes. Volatile losses as a percentage of the oil applied were relatively small over the long term, but were substantial in terms of short term losses immediately after application. Biodegradation of both total oil and individual oil fractions followed first-order reaction kinetics. A composite first-order

biodegradation rate coefficient of 0.003 day^{-1} was computed after compensation for volatilization.

Site monitoring determined that heavy metals were immobilized and the organic priority pollutants were degraded in the zone of incorporation (top 30 cm). Some build-up of metals occurred over the study period.

Operational considerations such as sludge loading rates and frequencies, proper tillage of the zone of incorporation, prevention of oil percolation and runoff, and operation of field equipment after sludge application are important factors in the design of land treatment facilities.

This report was submitted in fulfillment of Cooperative Agreement No. CR80757810 by the School of Civil Engineering and Environmental Science, University of Oklahoma under the sponsorship of the U.S. Environmental Protection Agency. The report covers a project period from April, 1980 to April, 1983 field and lab work was completed in June 1983.

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SECTION 1

INTRODUCTION

Land treatment of various wastes has been practiced world-wide for more than 100 years. Municipal wastes and sludges were probably the first such wastes to be spread on the land. This practice was no doubt influenced by the fertilizer value of these wastes. Many industrial wastes have also been applied to land for treatment and disposal. In the past 25 years, land treatment of sludges from petroleum refineries has become a more frequently used process. Recently, it was reported that 9 percent of the refinery sludges were disposed of by land treatment in 1973 with an increase to 34 percent projected by 1983 (Adams and Koon, 1977).

Work completed to date shows that land treatment can be an effective and environmentally safe procedure for oil and biological sludges. Migration of heavy metals can be controlled by maintaining aerobic conditions and a pH above 6.5 (Fuller 1977, Dibble and Barth 1979, Francsen 1980, and Huddleston 1979). One potential problem resulting from land treatment of refinery sludges is leaching of organics through the unsaturated zone to the ground water. Leaching is addressed in this study. When land area is readily available, land treatment is usually more cost effective than the other disposal techniques, including landfilling. The relative simplicity of the process is a major advantage. However, process simplicity can also lead to quick abuse. For example, the operator may not distribute sludge evenly over the land treatment site, but may discharge the contents of the tanks over the dike onto the site without distribution or entrainment.

When oil is applied to soil, losses occur through volatilization, downward migration, biodegradation and photodegradation. A high percentage of the volatilization takes place during and immediately after application and tilling. After a few days volatilization approaches a baseline level and decreases at a very slow rate for several months. Losses through volatilization and migration are undesirable, while losses through photodegradation and biodegradation are desirable. It is preferable to maximize the biodegradation process and minimize the rate of volatilization and migration to avoid environmental adversities. It is also important to know if any pollutants are released into the environment, beyond the limited soil treatment zone.

A review of the literature published relating to land treatment of petroleum industry residues was carried out. Site visits and personal interviews were also conducted for several refineries in Oklahoma. Limited information exists concerning site selection, site preparation, run-off control, and sludge application techniques. The response of crops in sludge treated areas and the relation of vegetation to the process, has also been reported.

Many questions about the process are unanswered. The most important questions relate to potential migration of constituents, basic design criteria for loading rates and application practices. Optimization of the process has not been completely defined. Site life, closure and unsaturated zone monitoring are also topics on which very little information exists. An increase in usage of land treatment processes and the strict regulations outlined in the U.S. Resource Conservation and Recovery Act, suggest the establishment of valid design guidelines for certain industries is urgently needed. Because petroleum refineries constitute one of the top ten industrial waste generators and was in 1981 among the fastest growing in the nation this study was undertaken.

The major objectives of the study are as follows:

(1) Determine the design criteria for the land treatment process as it applies to oily residues. The criteria are loading rates and application frequencies and tilling frequency.

(2) Study the fate of selected priority pollutants commonly present in oily residues.

(3) Assess the atmospheric emissions from land treatment application of oily residues.

To accomplish this study a land treatment research site was established near the University of Oklahoma campus. A total of 32 test plots and 8 control plots, each 6.0 m x 2.7 m (20 ft x 9 ft), were established. A 4 x 4 factorial experiment was proposed with loading rate and loading frequency as the two variables. Duplicate combinations of loading rates and frequencies were established.

The experimental design, including loading rates and frequencies, were modified as the study progressed. The final design is discussed in the appropriate sections of this report. The loading rates and frequencies were modified because of unfavorable antecedent soil conditions and climatic conditions. Higher than average rainfall made oil application and tilling impossible for months at a time. At the higher loading rates, it was not possible to apply all the sludge at one time because the soil became oil/water saturated and excess sludge would run off the plot. Therefore, applications at high loading rates were split and applied over two or more days. On some occasions, rain forced the second application to be postponed or eliminated, thus the loading rate/frequency for that plot was altered.

The soil of the zone of incorporation, top 30.0 cm (11.8 in) of the research plots was sampled for oil content, pH, moisture content, and nutrients usually just prior to application of oily residues. This sampling program was established so rates of degradation could be determined.

The fate of selected organic and inorganic priority pollutants was determined on two plots with loading rates of 10 percent and 6 percent, and at application frequency of 2 times per year. The plots were sampled 8 times in 15 months. The samples were analyzed for the priority pollutants suspected in the oily residues, as well as possible degradation products. Samples were collected from the top 30.0 cm (11.8 in) for such analyses. Samples were also taken below the zone of incorporation to detect which priority pollutants were migrating vertically.

In assessing atmospheric emissions from land treatment, the objectives were 1) to determine the rate and magnitude of fugitive hydrocarbon emissions from land treatment of refinery sludges, 2) to identify the relative effects of such parameters as sludge loading rate, temperature, soil moisture content and relative humidity on the magnitude of hydrocarbon emissions, 3) to identify and quantify individual compounds being emitted to the atmosphere, and 4) to develop a statistical model to predict the total volatile emissions rate based on the above mentioned variables.

Limited oil content monitoring from the unsaturated zone of heavily loaded plots was performed to determine the extent of migration of oil below the zone of incorporation.

Fractionation studies were conducted on two moderately loaded plots to investigate the loss kinetics of individual oil fractions. A fractionation scheme separated the recovered hydrocarbons into four fractions: saturates, asphaltenes, aromatics, and polar compounds.

From a process standpoint none of the individual plots reached equilibrium in two years. An estimate of four to five years is required to reach equilibrium. Therefore, an additional two to three years would be needed to more fully evaluate the land treatment process for equilibrium biokinetics. The biodegradation process for the study followed psuedo-first-order reaction kinetics for both total oil and individual oil fractions. A simplified single-substrate model was developed for possible use in process design and operation.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The project demonstrated that land treatment is a viable method for treatment of API separator sludge.
2. Annual loading rates should be based on projected equilibrium oil concentrations not exceeding 12 percent oil with an individual application maximum of 4 percent oil.
3. Soil should be tilled just preceeding application and then immediately following to increase the soil sorption and holding capacity, respectively.
4. Proper surface slopes are important to maintain adequate drainage and control erosion.
5. Rototilling under proper moisture conditions is important. Tilling under "wet" conditions resulted in undesirable physical changes while tilling under very dry conditions was not beneficial.
6. Losses of oil by degradation followed pseudo first-order kinetics.
7. Variation between sample replicates and detection-limiting concentrations hindered monitoring the fate of priority pollutant present in the applied waste.
8. Volatile emissions accounted for about 2/3 of the losses at application, but only approximately 6 percent of the total losses over a several month period. Hydrocarbon emissions did not exceed 1979 National Air Quality Standards.

RECOMMENDATIONS

1. Further studies to reinforce the projects findings should include optimization of tillage methods under variable soil moisture conditions and soil types.
2. The influence of climate variability of waste constituents in petroleum refinery sludges, potential for air pollution, long-term effects of waste application, closed site revegetation, and monitoring requirements are areas needing further research.
3. Full scale studies to determine waste generation, waste characteristics, storage, and land requirements are recommended.

SECTION 3

LITERATURE REVIEW

The petroleum refining industry generates large amounts of waste each year, a sizeable proportion of which is classified as hazardous. Galloway (1979) reported on an EPA survey which placed the amount of hydrocarbons in refinery solid wastes at 169,465 metric tons per year.

The individual process streams which contribute to this quantity are listed below (Rosenberg et al., 1976).

1. Crude tank bottoms - solid sediment from incoming crude oil, which has accumulated at the bottom of the crude oil storage tanks.
2. Leaded or non-leaded tank bottoms - solids which settle to the bottom of product tanks.
3. API separator sludge - solids which settle in the API separator during primary wastewater treatment.
4. Neutralized HF alkylation sludge - alkylation sludge produced by both the sulfuric acid and hydrofluoric acid alkylation processes.
5. Kerosene filter clays and lube oil filter clays - clays used to remove color bodies, chemical treatment residues, and traces of moisture from product streams.
6. Once-through cooling water sludge - sludge from primary settling tanks used for cooling water.
7. Dissolved Air Flotation (DAF) float - generated

when dissolved air flotation is used to remove oil and solids from wastewater streams.

8. Slop oil emulsion solids - solid fraction of oil skimmed from API separators.
9. Spent lime from boiler feedwater treatment.
10. Cooling tower sludge - sludge which settles out in the cooling tower basin.
11. Exchanger bundle cleaning sludge.
12. Waste biosludge - excess sludge from biological treatment of refinery aqueous waste streams.
13. Storm water silt - silt which collects in the stormwater settling basins.
14. Fluid Catalytic Cracker (FCC) catalyst fines - generated when catalyst is regenerated by burning off coke produced during usage of the catalyst. Collected by electrostatic precipitators or similar pollution control devices.
15. Coke fines.
16. Spent catalysts.
17. Chemical precipitation sludge - produced when chemical coagulation is used to remove suspended matter from aqueous waste streams.
18. Vacuum filter or centrifuge cake.
19. Silica gel - used to remove water from instrument air.

DAF float, slop oil emulsion solids, heat exchanger bundle cleaning sludge, API separator sludge and leaded tank bottoms are classified as hazardous by the Environmental Protection Agency (CFR Title 40, July 1982).

Table 3.1 lists the characteristics of some refinery solid wastes. The wastes with highest oil content are API separator sludge, DAF float, tank bottoms and vacuum filter sludges.

TABLE 3.1. CHARACTERISTICS OF REFINERY SOLIDS WASTES

	Typical Composition, Percent				
Waste Type	Oil or Hydrocarbon	Water	Volatile Solids	Inert Solids	Characteristics
API Separator Sludge	15	66	6	13	Fluid slurry of oil, water and sand
Tank Bottoms	48	40	4	8	Oil-water mixture
Chemical Treatment Sludge	5	90		5	Slightly viscous fluid
Air Flotation Froth	22	75		3	Thick, oily fluid
Precoat Vacuum Filter Sludges	22	29		49	Temperatures
Biological Treatment Sludges					
Raw	0	98	1.5	0.5	Water Consistency
Mechanically Thickened	0	94	4	2	Thick, but pumpable
Centrifuged	0	85	10	5	Viscous-peanut butter consistency
Vacuum Filtered	0	75	15	10	Wet crumbly solid
Screw Pressed	0	40	40		Intact, solid cake
Water Treatment Sludge	0	95		5	Pumpable fluid, sometimes gelatinous

Cross, F.L. and J.R. Lawson, "A New Petroleum Refinery". American Institute of Chemical Engineering Symposium Series, Vol. 70, No. 136, P. 812.

Land Treatment Management Practices

Several researchers have investigated land treatment of oily residues in the last few years. These include Kincannon, 1972; Raymond, Hudson and Jamison, 1976; Cresswell, 1977; Odu, 1978; Dibble and Bartha, 1979; Meyers and Huddleston, 1979; Huddleston, 1979; and Lewis (undated).

Kincannon (1972) evaluated land treatment of three different oily wastes during an 18 month project. Three sludges, crude oil tank bottoms, a high molecular weight fuel oil and a waxy raffinate were investigated. Three test plots for each sludge were evaluated.

For a given sludge each test plot was treated identically except for soil nutrient additions. Fertilizer additions ranged from zero to heavy. The plots were located within the Shell Oil Company refinery at Deer Park, Texas. The plots were located in an area where oil wastes have been previously disposed on the land, thus residual oil was initially present in the soil. Fertilizer additions were based on agricultural experience. Initially, nitrogen was added to the test plots in quantities if 1,000;500; and 0 pounds per acre (urea). Similarly phosphorous (calcium hydrogen phosphate) was added at rates of 200;100; and 0 pounds per acre (P_2O_5). Further nutrients were added to the plots during the study. No attempt was made to grow crops on the plots.

Residual oil in the soil was approximately ten percent as a result of previous use of the soil area for oily waste disposal. The oil content of the soil returned to approximately residual levels within six to seven months of application, but was not observed to decrease below this point. Oil disappearance rates were greater for those plots where fertilizer was added than where no fertilizer was used. Oil removal rates markedly slowed in winter. Analyses of metal content in the soils was inconsistent and no conclusions were possible. Analyses of soil cores indicated oil and nutrients did not infiltrate to the 2, 4 and 6 foot depths. Oil was present at the 2 foot depth at the start of the study.

The author concluded both aromatic and saturated hydrocarbons were reduced with time in the soil for crude oil tank bottoms and bunker fuel oil. Organic acids were absent from the oil added to the soils but present in each sample of the extracted oil. The total saturates simultaneously decreased.

Other general project observations include:

1. Major species of microorganisms present are members of the genus Pseudomonas, Flavobacterium, Nocardia, Corynebacterium and Arthrobacter.
2. Rainfall runoff water contained 30 to 100 ppm oil.
3. Cost of soil cultivation was estimated to be $3.00 per barrel of sludge at 33 percent oil.

Raymond, Hudson and Jamison (1976) reported on a study in which six oils were subjected to land treatment. The oils used were: crankcase oils from cars, used crankcase oil from trucks, Arabian heavy crude oil, Coastal Mix crude oil, home heating oil No. 2 and residual fuel oil No. 6. The oils were tilled into 10 to 15 cms of soil, with monthly tilling for the first three months followed by quarterly tilling afterwards. Reduction in oil concentration , 48.5 to 20 percent, and rates of degradation up to 2.4 $m^3/4x10^3$ m^2 per month were observed. No oil loss via water movement was observed in run-off, leachate or soil. Vegetative growth was still inhibited nine months after application. Significant increases in hydrocarbon utilizing microorganisms were observed in all treated plots.

The authors noted problems in obtaining good mixing of oil and soil, resulting in variability in the analytical results. No great differences in degradation of alkanes and aromatic compounds were observed.

There are essentially three ways of disposing of these refinery solid wastes. These are landfilling, incineration and land treatment. Of these three, land treatment is rapidly becoming the most popular, because it is relatively inexpensive (Grove 1978), and is thought to be environmentally safe. Incineration is expensive, while landfilling does not treat the waste, but merely stores it in the ground, where it becomes a potential source of ground water contamination.

Disposal of oily residues by land treatment has been practiced for the last 20 to 25 years, but has only become widely used since around 1970. In this method, the wastes are applied to the soil, tilled or disced into the top 15 to 20 cms (10 to 6 in), nutrients added, and allowed to biodegrade.

Cresswell (1977) identified the primary factors affecting the degradation of oily residues as:

(1) petroleum composition
(2) temperature
(3) nutrients
(4) oxygen availability
(5) water content of soil
(6) soil pH.

Cresswell found that biodegradation was a relatively slow process, and a loading rate of 5 percent in the top 6 inches of soil will result in the degradation of about 60 barrels of oil/acre/year. Paraffinic oils are more rapidly degraded than asphaltic oils. He found for oil concentrations under 10 percent, the mass of oil degraded per unit mass of soil increases with increasing oil concentration. Management practices consisted of rototilling the top 6 inches of soil monthly, and maintaining ammonium nitrogen and orthophosphate levels above 50 mg/kg and 30 mg/kg, respectively.

Meyers and Huddleston (1979) reported on field work on land treatment of oily residues. They added fertilizer to achieve C:N ratios of 1:400 and 1:800, and a C:P ratio of 1:5000. No difference in the rate of degradation was noted between plots with the two C:N ratios during the first year of the study. The amount of nitrogen added was doubled in the second and third years of the study, to ensure that enough was being added to the soil. The authors found all oil fractions were degraded at low (5 percent) loading rates. Plant cover could be maintained to maximize oil degradation at this loading rate. Tilling became more important at higher loading rates.

Huddleston (1979) in a general review of land treatment describes the advantages of land treatment as:

(1) effectiveness of a comparatively reasonable cost,
(2) relative environmental safety,
(3) use of natural processes that recycle the waste,
(4) process simplicity,
(5) possible improvement of soil structure and fertility.

He identified the major operational parameters as:

(1) controlling pH between 7 and 9,
(2) oil content loading of between 5 and 10 percent,
(3) moisture content of soil between 6 and 22 wt percent depending on soil type i.e. between 50 and 80 percent of soil water-holding capacity,

(4) blending of waste and soil by tilling or discing every 4 to 8 weeks.

Dibble and Bartha (1979) monitored oily sludge degradation by CO_2 evaluation and analysis of residual hydrocarbons. They identified the following parameters as important in optimizing the process:

(1) soil water holding capacity of 30 to 90 percent,

(2) pH of 7.5 to 7.8,

(3) C:N and C:P ratios of 60:1 and 800:1, respectively,

(4) temperature of 20°C or above,

(5) application rate of 5 percent wt/wt oil in soil,

(6) frequent small applications rather than a single large application.

They also found that the addition of micronutrients and organic supplements was not beneficial to the degradation process.

Lewis reported on sludge farming at Exxon's Bayway Refinery and Chemical plant. Plot studies at this plant indicated that loadings of 150 tons/acre/year of oils and solids were possible without overloading the soil or producing any oil run-off contamination. The management techniques used consisted of:

(1) Maintaining a soil pH of 7.0 to 7.5.

(2) Maintenance of nitrates and phosphates at 20-30 mg/kg by applying commercial fertilizer 2 to 3 times per year.

(3) sludge applications to the top 6 inches of soil to achieve an oil content of 8-9 percent. The oil content was allowed to decrease to 2-4 percent before the next application of sludge.

(4) Weekly discing of the till zone to promote oil

degradation.

The author notes that the management practices described above resulted in a loading rate of 450 tons per acre of oil solids and water, or 100 tons per acre of oil alone.

Microbial Degradation of Oil Fractions

Johnson, Cook and Westlake (1972) in a study of crude oil utilization by bacteria, found that the saturate fraction was used preferentially by the microorganisms. In another study in 1979, Jobson et al., showed that the use of fertilizers increased the rate of utilization of the saturate fraction as well as the bacterial count.

Cansfield and Racz (1978) reported degradation of all components of hydrocarbon residues from crude oil storage tanks. Of the total residues applied, 50.4 percent were degraded in 833 days. Saturates were degraded 54.6 percent, monoaromatics 50.5 percent, diaromatics 57.1 percent, and polyaromatic and polar compounds 44.4 percent. High molecular weight material such as asphaltenes only degraded 11.1 percent. They reported that the alkanes degraded to low levels in the first 106 days. The polar fraction increased and then decreased. This speculated that degradation of all fractions would occur through the formation of polar compounds.

Davis (1967) also reported work showing paraffinic hydrocarbons (alkanes) in the medium molecular weight range were oxidized more readily than either low molecular weight paraffins, or heavy paraffinic fractions. Aromatic fractions were more difficult to degrade than paraffins.

Westlake et al., (1978) investigated in-situ degradation of oil in a soil of the boreal region of the

Northwest Territories. Replicate plots were used for this study. Fertilizer and bacteria were applied with the oil. In fertilizer applied plots there was a rapid increase in bacterial numbers. The saturates content of fertilizer applied plots decreased with time. Treatment of plots with oil degrading bacteria did not accelerate the rate at which chemical changes in recovered oil occurred. The reason given for this phenomenon was the concentration of indigenous oil degrading bacteria in these soils was high compared to the concentration of bacteria introduced.

Two studies by Huddleston and Cresswell (1976) at Billings, Montana and Ponca City, Oklahoma on degradation of oily residues revealed degradation of oily residues progressed, there was an increase in the percentage of resin-asphaltenes, and a decrease in the percentage of paraffins and aromatics. The Billings study showed that 70 percent of the applied oil was lost over an 18 month period, with the percentage of resin-asphaltenes in the remaining oil increasing from 20 to 60 percent. The Ponca City study revealed a similar trend, with a 35 percent loss of applied oil occurring over a 24 month period, and the percentage of resin-asphaltenes in the remaining oil increasing.

Walker, Colwell and Petrakis (1976) studied the biodegradation rates of petroleum by monitoring the changes in the concentrations of saturates, aromatics, resins and asphaltenes over time. The results showed that the concentration of saturates decreased steadily, while the concentration of resins and asphaltenes increased over time. The aromatics concentrations decreased, leveled off and then increased again.

Fate of Metals in Land Treatment of Oily Residues

Most of the land treatment studies have focused on short-term effects. Few researchers have evaluated the potential for long-term impacts on the environment. These impacts need to be addressed in view of the buildup of heavy metals in the soil during land treatment. Fuller (1977) reported that under anaerobic conditions the mobility of several heavy metals (As, Cr, Fe, Cu, Zn) is enhanced. (Anaerobic conditions can and do occur at land treatment sites, particularly under conditions of high soil moisture content, when leaching is most likely to occur.)

Hahne and Kroontje (1973) reported that in the presence of chloride ion, the solubility of Cd, Zn, Pb, and Hg is increased even at a pH of 9. They indicated that at a pH of 9 soluble chloride complexes can be found at ion concentrations of 354 and 28 ppm. High chloride ion concentrations can be present at land treatment sites because of the occurrence of brines with crude oil and the high chloride ion content of some wastes from refinery operations.

Soils used for the disposal of oily sludges may contain a number of heavy metals which are potentially toxic to the environment. Contamination of ground water by heavy metals is believed to be of minimal concern if adequate soil pH is maintained at a land treatment site. Most metals are immobilized when the soil pH is greater than 6.5. The leaching of metals is therefore not of major concern at treatment sites with proper pH control (Dibble and Bartha 1979, Francsen 1980, and Huddleston 1979).

Leeper (1978) believes that pH is the single most important aspect of the reaction between heavy metals and soils. Soil treated with sludges containing heavy metals should be medium to fine textured, have a pH above 6.5 and contain 3-7 percent organic matter with a Cation

Exchange Capacity (CEC) of at least 14 in order to be considered acceptable for the retention of metals (Huddleston 1979, Leeper 1978, Loehr 1979).

Hydrocarbon Processing (1980) reported that "virtually all published information on landfarming indicated that there is little migration of contaminants below the top 30 cm (12 in) of soil". To date little work has been done on leaching of metals in soil containing oil wastes, although the movement of heavy metals in landfills or in soils amended with sewage sludge has been studied extensively (Schilesky, 1979). The possibility of heavy metals leaching through soil is great if high pH levels are not maintained at land treatment sites. Heavy metals can be toxic, therefore, suitable oily wastes for land treatment are those which do not contain extremely high metal concentrations (Huddleston, 1979).

Raymond, Hudson and Jamison (1976) conducted a land treatment study in which oil degradation was monitored over a one year period. The movement of lead, which was the metal of highest concentration in the oil, was examined and no evidence was found that the nitric acid-soluble form had leached through the soil. Dibble and Bartha (1979) found hydrocarbons did not leach below a depth at which oil sludge was mixed with sandy soil. Based on Raymond et al.'s studies, Dibble and Bartha concluded that heavy metal residues from oil sludges would display low mobility in limed soil. Huddleston et al., (1982) reported in a study carried out at five closed refinery land treatment sites that wastes had been degraded without appreciable migration of degradation products, and that metals in the waste remained in the application zone.

One problem that might arise from the disposal of oily residues by land treatment is the movement of leachate through the unsaturated zone to the underlying ground water, resulting in contamination of the ground water. Thus, the unsaturated zone at a land treatment site needs to be monitored in order that any pollutant movement can be detected. Current EPA regulations require the use of GW monitoring wells, and the collection and analysis of soil core samples as a method of detecting pollutant movement. EPA has also required the use of soil moisture samplers for sampling soil pore water in the unsaturated zone under active land treatment sites.

Soil moisture samplers using a porous ceramic cup have been used for many years for collecting soil pore water samples. Briggs and McCall first reported on the use of porous ceramic cups in 1904, and since that time, their usage has increased considerably. However, with their increased usage, questions have arisen as to the validity of samples collected in this way.

Wagner (1962) used the porous ceramic cup and reported no adsorptive capacity of the cup for nitrate ions, but an appreciable adsorptive capacity of about 1 mg of N for NH_4^+ ions. Reeve and Doering (1965) used ceramic cups to collect soil water samples for salinity determinations. The values obtained from the sampler agreed with the values obtained by the conventional saturation method. They also found that the composition of the sample changed with time, but that consistent and reliable values for the composition of the soil solution were obtained when a vacuum in the range of 0 to 500 millibars was used to collect the sample.

Grover and Lamborn (1970) reported that ceramic cups contributed excessive amounts of Ca^{++}, Na^+ and K^+ to solutions drawn through them, and adsorbed phosphorus from solutions containing phosphorus. They found that leaching the cups with 1 N HCl reduced Na and K contamination, and the amount of phosphorus adsorbed, but appreciable amounts of calcium contamination still occurred. Wood (1973) also reported contamination of samples by Ca^{++}, Mg^{++}, Na^{+}, HCO_3^- and SiO_2. He minimized the problem by leaching the ceramic cups with 8 N HCl.

Zimmermann, Price and Montgomery (1978) reported loss of nutrients after filtration through porous ceramic cups used to sample sediment. The most significant losses occurred with HN_4^+ and $PO_4^{\equiv}$ ions. Levin and Jackson (1977) also reported loss of NO_3^--N when they used porous ceramic cups for sampling soil water.

Johnson and Cartwright (1980) used soil moisture samplers with porous ceramic cups for sampling the unsaturated zone under landfills in Illinois. They found that samples taken with soil moisture samplers were representative of the surrounding leachate composition of major ions. They pointed out that while sample variability or bias of several milligrams per liter may be quite significant when the concentration of the ions of interest in the soil water is low, this is not the case when sampling highly contaminated leachate with high ionic concentrations.

England (1974) pointed out the following:

(1) Concentrations and composition of the soil solution are not homogeneous throughout its mass.

(2) Cations vary widely in the degree of dissociation from the surface of electronegative colloidal particles. Water drained from large pores at low suctions may have a different chemical composition from that extracted from micropores.

(3) Concentrations of various ions in a soil solution generally do not vary inversely with the soil water content. Dissolved quantities of

> some ions increase with increasing soil moisture while quantities of other ions may decrease.

Hansen and Harris (1975), did extensive work on the use of porous ceramic samplers. They found that the rate of sample uptake was strongly influenced by cup uptake rate, plugging of the cup, sampler depth, and the type of vacuum system used. They also found that a number of factors affected the sample concentration as the sample was drawn through the ceramic cup. These factors were intake rate, leaching, sorption and screening.

Van der Ploeg and Beese (1977) showed that the soil moisture sampler distorts the existing gradient patterns in the soil in such a way, that around the ceramic cup exaggerated percolation rates are created. They state that the composition of the collected sample is not representative for one particular depth, but reflects some average composition of the surroundings. Van der Ploeg and Beese found that extraction rates with even a small vacuum applied, were much higher than the percolation rate under freely vertically draining conditions. They could find no relation between the amount of soil water extracted and the freely percolating soil water.

A great deal of care must be taken in extrapolating results obtained with the use of soil water samplers to conditions which actually exist in the unsaturated zone. This is especially true when dealing with environments where solute concentrations are low. Little has been written on the effect of the ceramic cups on low organic concentrations which may be present in the soil water, and this is an area which needs more research.

Despite these reservations, these samplers are currently one of the best methods of monitoring the movement of pollutants in soil pore water at land treatment sites.

They have a number of advantages:

(1) They can be installed under the active portion of land treatment sites, and monitored off site.

(2) They are relatively inexpensive to install, and do not require highly trained personnel to use them.

(3) The sampler itself is inexpensive.

A soil moisture sampler commonly used in monitoring the unsaturated zone is a pressure vacuum model which was developed by Parizek and Lane (1970). This sampler can be effectively used up to depths of 50 feet, and can be used to collect samples over a long period of time.

Volatile Emissions

A review of the literature dealing with land treatment of oil residues did not reveal much information on volatile organic emissions from the process. Three sources, however, contained information about volatile organic emissions from land treatment of refinery sludges.

Minear et al., (1981) conducted a study to assess the atmospheric emissions from the land treatment of refinery sludges. This study was jointly funded by the American Petroleum Institute and the U.S. Environmental Protection Agency (EPA). These researchers developed a small laboratory unit to simulate land treatment operations. The effects of certain variables on emission rates such as sludge type, sludge volatility, soil moisture content, wind speed, relative humidity, air temperature, soil temperature, sludge loading rate and the method of sludge application were studied. The authors found that sludge volatility, sludge loading rate, application method and soil moisture content were important parameters affecting emission rates. API separator and tank bottom sludges were used in this study. The results of this study showed that the hydrocarbon concentration in the air rose sharply during or shortly after sludge applications.

The concentration was at a maximum for less than five minutes, and then decreased to a relatively low level within 30-36 minutes from the time of sludge application. Sludges with different volatilities were used, and the weight percent of applied sludge lost in 30 minutes varied from 0.07 to 3.2, depending on the sludge.

Minear et al., found the addition of gasoline to the sludge increased the emission rate, while water addition had no effect on this rate. Subsurface injection and delaying tilling for a while after application of sludge were recommended as ways of minimizing emissions. Minear et al., also showed that increasing soil moisture increased the amount of hydrocarbons emitted, but heating the sludge before application had no effect on the emission rate. Air velocity did not affect the total quantity of hydrocarbons emitted, only the rate of emission.

Francke and Clark (1978) conducted land farming experiments at Oak Ridge National Laboratory to evaluate a biological assimilatory process for disposal of waste oil and machine coolant. They applied oil and fertilizer to a 0.005 hectare (0.088 acre) plot, tilled to a depth of 15 cm (6 in) and cultivated regularly for 4 months. Average oil application rate was 0.154 liters per cubic meter (1.15 gallons per cubic foot) of soil. Decomposition rate of oily waste was reported to be 24 kg/m^3 (1.5 lb per cubic foot) of soil per month; decomposition rate of coolant was reported to be 71 kg/m^3/month (4.45 lb/ft^3 month).

They also conducted laboratory tests to determine the hydrocarbon evaporation rate from the test plots. Total evaporative losses from actual test plots over the 53 day test period were calculated to be about 31.8 liters (8.4 gallons), equivalent to less than 0.1 percent of the total oil applied.

Laboratory tests were also conducted to determine the evaporation rate from the machine coolant. Estimated losses during the 78 day test period were 110-140 liters (29-37 gallons), less than 0.6 percent of the total oil applied. The author reported that the primary evaporative constituents were those identified with oils and coolants.

Volatile Organic Compound (VOC) emissions from a land treatment operation of petroleum sludge were studied by the Suntech group (undated). API separator sludge containing about 5 weight percent oil, and centrifuge sludge containing about 8 weight percent oil were land-treated.

Centrifuge sludge was spread and tilled and volatile organics were measured during a 13 day period. Volatile organic compound emissions averaged about 594 kg/ha (530 pounds) of hexane equivalent per acre, or approximately 46 kg/hectare/day (41 pounds per acre per day). Total emissions were reported to be about two weight percent of the oil applied.

Spreading of API separator sludge resulted in VOC emissions of 2196 kg of hexane equivalent/hectare (1960 pounds per acre), or 85 kg/ha/day (76 pounds per acre per day) which represented about 11 weight percent of the oil spread. Tilling after spreading increased VOC emissions to 2357 kg/ha (2103 pounds per acre), or about 14 weight percent of the oil spread.

Tilling and high temperature increased the emission rates from both types of sludges. Tilling was not a factor over an extended period, although it initially increased emissions.

Stearn, Ross and Morrison (1977) conducted a literature review relating to oily waste decomposition, volatilization, migration through soils, and interaction with the environment when oily waste was disposed on land. Four case studies were performed to determine if the method was practical and environmentally acceptable.

The results of this review showed that the degree of oil loss by volatilization is related to the vapor pressure of hydrocarbons, soil porosity, tortuosity and surface absorption characteristics of the soil. Hydrocarbons with high vapor pressures, such as propane, evaporate before outward migration or biological oxidation occurs in soils. However, lower vapor pressure hydrocarbons, such as heavy oils, residual fuel oils, grease, solid paraffins and high molecular weight asphaltenes; migrate or biologically oxidize before evaporation. Using information from the literature, the authors estimated that for highly volatile hydrocarbons deposited in soil to a concentration of 0.1 g/cm^3, it would require approximately one month for all oil in the top 4.6 cm (1.8 in) layer to evaporate. Further, for a heavier fuel oil, with a contamination zone depth of 9.8 inches, approximately 6 percent of the oil would evaporate in two years. The range of time constants relevant to biological oxidation of oil is estimated between two and twenty months. Therefore, the oil evaporation rate is insignificant as compared to the biological oxidation rate.

The authors reported that relative amounts of evaporated versus biologically oxidized oil can be affected by the disposal methods employed. For any hydrocarbon having a vapor pressure less than 100 mm of mercury, the ratio of evaporation to biological oxidation can be minimized by maximizing the depth of plowed zone if the soil is not completely saturated with water. Although this procedure will decrease the biological degradation rate, it will decrease the evaporation rate even more.

Chamber techniques to measure the gas transfer across the soil-atmosphere interface have received considerable emphasis the past few years. Matthias, Blackmer and Bremner (1980) described a chamber technique for field measurement of emissions of nitrous oxide from soil. The researchers placed an insulated cylindrical metal chamber (diameter 88 cm; height 17 cm) over the soil surface for 20 minutes and collected air samples in 1 liter evacuated glass bottles fitted with glass stopcock in 5 minute intervals. A rotary valve pump was used to evacuate each sample bottle to a pressure of <.1 mm Hg. A windbreak was used to minimize wind-induced movement.

The air samples then were analyzed for nitrous oxide (N_2O) within 24 hours by a gas chromatographic procedure. The rate of nitrous oxide emission was calculated from the increase in the concentration of nitrous oxide in the air within the chamber.

The effects of wind break, insulation, air pressure fluctuation and mixing air within the chamber were studied. The authors reported that the concentration of nitrous oxide in air within the chamber increased linearly with time on calm day; however, it did not increase linearly with time on windy days. The effect of insulation showed that the temperature perturbation of air within the insulated metal chamber was very small compared with the perturbation observed within the metal and plexiglass chambers. Since temperature has a very significant effect on the rate of microbial activity and the resulting nitrous oxide emission from the soil, extensive tests showed that the above described chamber would not significantly affect the soil temperature.

The authors used an electric fan to mix the air within the chamber. The repeated tests revealed that there was no significant difference between results obtained with and without using a fan.

Studies by Kimball and Lemon (1971-1972), have shown that air-pressure fluctuations caused by turbulent movement of air over the soil surface may affect gaseous mass flow within the soil. However, Matthias et al., (1980) reported that air-pressure fluctuation induced by withdrawing and reinjecting air over the soil did not significantly affect the rates of N_2O emission at various sites using the chamber technique. According to Matthias, the chamber technique has the important advantage of not significantly disturbing the structure or the environment of the soil under study.

SECTION 4

DESIGN AND OPERATION OF THE LAND TREATMENT SITE

SITE SELECTION

The ten acre site selected for this study is located on university property adjacent to the east right-of-way of Interstate Highway 35 and immediately north of Westheimer Field, the University Airport. More specifically, it is located in the Southwest quarter, of the Northeast quarter, of Section 14, Township 9 North, Range 3 West, Cleveland County, Oklahoma. Figure 4.1 shows the location of the site. The site is owned by the University of Oklahoma. The climatic conditions in this area can be described as mild winters and hot summers. The winters and springs during the period of the project were unusual in that rainfall was significantly above average for the duration of the project.

The following criteria represent the major considerations in selecting the location of the research site:

- The site should be owned by the University of Oklahoma.
- The site could have no past history of oil applications.
- A long term commitment of the site for use in research must be available.
- The site should be remotely located relative to urban population.
- The surface slopes should be mild to prevent erosion but at least 1 percent to provide

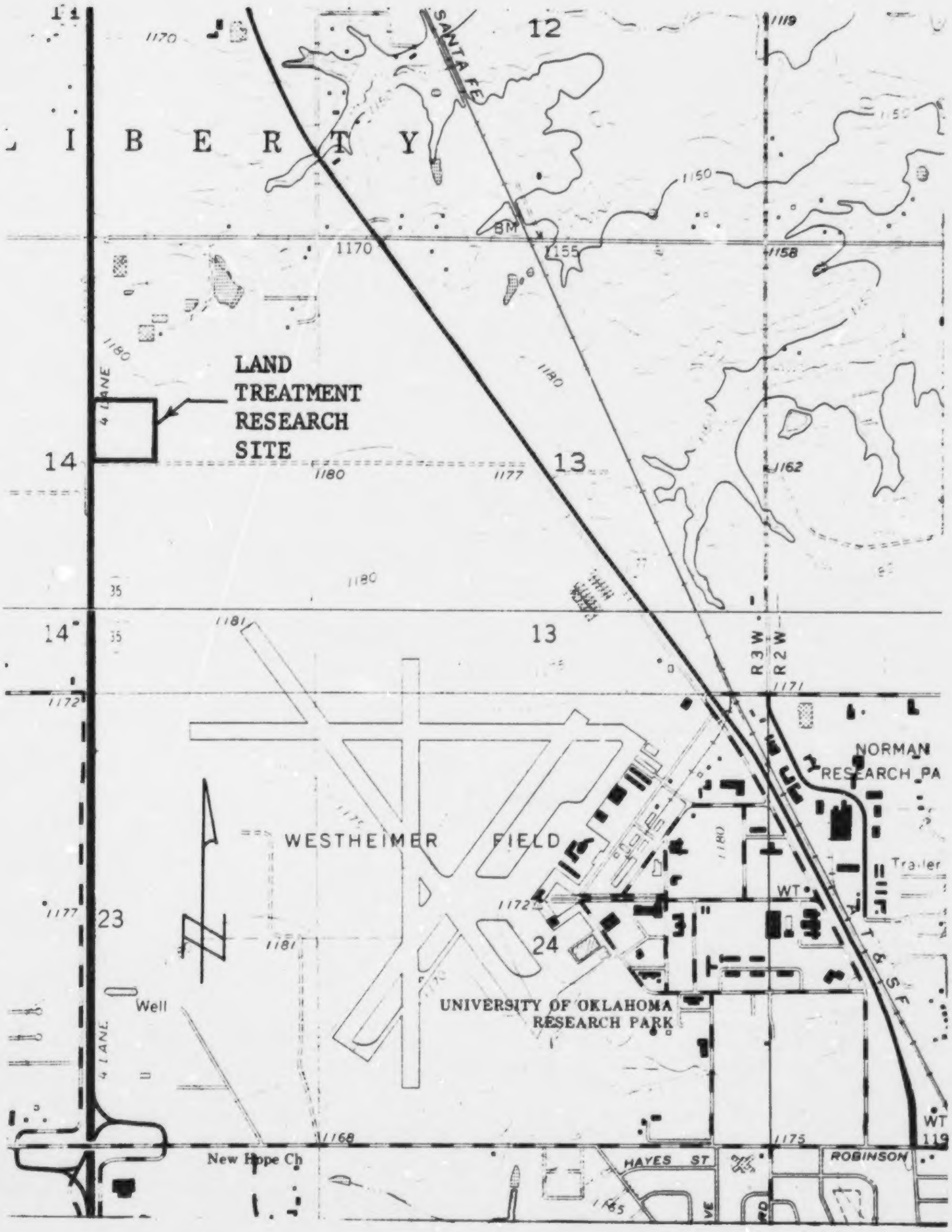

LAND
TREATMENT
RESEARCH
SITE
L I B E R T Y
SANTA FE
WESTHEIMER FIELD
UNIVERSITY OF OKLAHOMA
RESEARCH PARK
NORMAN
RESEARCH PA
New Hope Ch
HAYES ST
ROBINSON
4 LANE
Well
Trailer
R3W
R2W
12
13
14
23
24
1170
1180
1177
1181
1172
1168
1175
1158
1162
1155
1150
1171
1119
BM
WT

Figure 4.1. Land treatment research site location.

proper drainage.

- An impermeable clay should underly the site and maximum vertical separation from any fresh water aquifer must be provided.
- The surface soils should represent good agricutural soils with lateral uniformity.
- Reasonable road access and economic access to water and electric utilities is needed.

The site selected could not be directly serviced with a water supply without great expense. With this exception the research site meets all of the above criteria.

SITE DESCRIPTION AND CHARACTERISTICS

The Cleveland County Soil Survey defines the surface soils at the site to be part of the Bethany Silt Loam series. A reprint of the survey description of this soil series is as follows (Soil Conservation Service, 1960):

Bethany silt loam, (Bb)

This dark deep noncalcareous soil of the prairies is not extensive but occupies a few fairly large areas totalling 15,200 acres northwest of Norman. Surface and internal drainage are both very slow, but the soil is adequately drained for all crops commonly grown. It has a high water holding capacity and absorbs most of the precipitation, but crops are sometimes damaged during long droughts. One reason is that plants are unable to obtain water fast enough from the clay in the lower subsoil layers when the soil moisture content is low. Slope is less than 1 percent, therefore erosion is not a problem.

The surface soil, to a depth of about 38 cm (15 in), is a dark grayish-brown or dark-brown granular slightly acid silt loam that tends to crust on drying but is easily kept loose and granular under a wide range of moisture condition. The surface soil grades into the upper subsoil, a dark-brown or grayish-brown porous granular soil soil of slightly acid silty clay loam. This upper subsoil, 10 to 20 cm (4 to 8 in) thick, is neither tight nor hard, even when extremely dry, and is easily penetrated by moisture, air and plant roots. The upper subsoil grades into a lower subsoil of brown firm blocky clay that continues with little change to depths of 102 to 127 cm (40 to 50 in). Next in profile is brown heavy noncalcareous clay mottled with yellow and reddish brown, which grades at depths of 183 to 244 cm (6 to 8 ft) into alkaline to calcareous reddish silty clay or silty shale. This shale may be residuum of ancient water-laid materials.

Soil Analysis

Composite samples of the top eight 20 cm (8 in) of soil from the site were collected for gradation analysis. Samples were collected in a manner to establish variation in gradation of surface soils across the site. Gradation analysis were performed in accordance with AASHTO T88-72, Standard Method for Particle Size Analysis of Soils which includes hydrometer analyses for the fine soil particles. Results of the analyses are presented in Table 4.1.

TABLE 4.1. GRADATION ANALYSIS OF SURFACE SITE SOILS

General Description of Sample Relative to the South 1/2 of Site	Sample Depth (cm)	% Sand	% Silt	% Clay	Textural Classification
1-A-East 1/2	20	4.5	78.0	17.5	Silty Loam
1-B-East 1/2 (1-A split)	20	3.7	79.3	17.0	Silty Loam
2-A-East 1/2	20	3.9	78.6	17.5	Silty Loam
3-A-West 1/2	20	4.3	77.2	18.5	Silty Loam
Average Results		4.1	78.3	17.6	Silty Loam

The maximum variation found is within the limits of analysis error and indicates that the surface soil in the research area is of uniform texture. The top 12 inches of surface soil is of primary interest, as it represents the zone of incorporation for the land treatment process.

The samples described in Table 4.1 were further analyzed to determine their maximum densities at optimum moisture content and their plasticity characteristics. The "Harvard Miniature" procedure was used in the density measurements. The liquid limit test was conducted in accordance with AASHTO T89-76, Standard Method for Determining the Liquid Limit of Soils. Plastic limit and plasticity index procedures as described in AASHTO T90-70, Standard Method for Determining the Plastic Limit and Plasticity Index of Soils was followed. Results of these tests appear in Tables 4.2 and 4.3 below.

Uniformity of the surface soils on the site is further established by the low variation in the density and plasticity data. This soil is plastic over a small range of moisture contents (Table 4.3) indicative of the high silt and relatively low clay content of the surface soil.

TABLE 4.2. DRY DENSITY - OPTIMUM MOISTURE ANALYSIS RESULTS

Sample Identification	Sample Depth (cm)	Maximum Dry Density (PCF)	Optimum Moisture Content (%)
2-A	0-20	107.5	15
3-A	0-20	108.0	14
Average Results		107.7	14.5

TABLE 4.3. PLASTICITY ANALYSES

Identification	Sample Depth (cm)	Liquid Limit (%Moisture)	Plastic Limit (%Moisture)	Plasticity Index (%Moisture)
1-A	0-20	23.0	21.5	1.5
1-B	0-20	23.7	21.0	2.7
2-A	0-20	24.1	20.0	4.1
3-A	0-20	23.9	20.8	3.1
Average Results		23.7	20.8	2.9

Several shallow soil cores, approximately five feet deep were taken across the site. In addition, shavings from four deep site cores air drilled to 30.5 m (100 ft) were examined. Inspection of deep core materials further indicated that uniformity exists in the underlying strata. A general description of the typical soil profile beneath the site is given in Figure 4.2.

Clay material underlying the silty loam on the surface was found to have a coefficient of permeability less than 10^{-7} cm/sec. Underlying clay gradually changes to red clay shale at approximately sixty inches. Red shale continues to 30.5 m (100 ft) where drilling ceased. Thin lenses of sandstone 3 to 5 cm (1 to 2 in) were encountered at various positions in the shale beds.

No ground water table was encountered in any of the deep core holes. Known area hydrogeology indicates the only major aquifer water table to be approximately 154 m (500 ft) deep or deeper in the vicinity of the site (25). The soil pH ranged from 6.5 - 8.5.

SITE DESIGN AND CONSTRUCTION

The site was designed to hold a maximum of 50 plots, 2.7 m x 6 m (9 ft x 20 ft). Twenty foot buffer zones

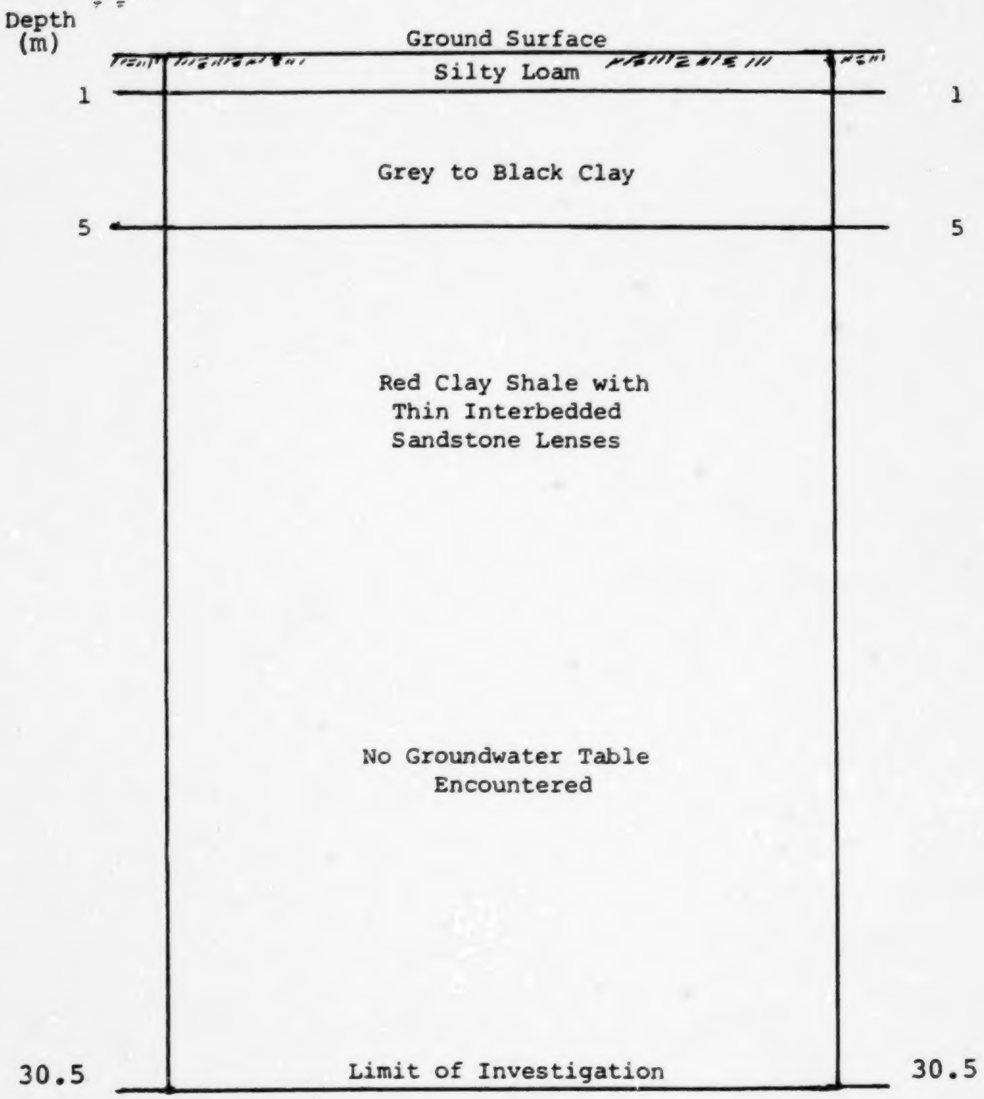

Depth
(m)
Ground Surface
Silty Loam
1
1
Grey to Black Clay
5
5
Red Clay Shale with
Thin Interbedded
Sandstone Lenses
No Groundwater Table
Encountered
30.5
Limit of Investigation
30.5

Figure 4.2. Typical vertical soil profile at site.

were provided between plots to minimize material transfer between plots. This spacing also made it convenient to maneuver the tractor, tiller, and applicator to each plot.

The entire site was diked to prevent surface water run-on to and run-off from the active site. A retention pond designed to retain run-off from a twenty-five year, twenty-four hour storm was constructed inside the diked area. Figure 4.3 shows the layout of the land treatment facility. Four ground water monitoring wells were installed; one upgradient, and three downgradient of the ground water flow. The ground water flow in this location is from east to west. Each well was 30.5 m (100 ft) deep.

The site was equipped with two tanks for storage of oil refinery sludges with a total capacity of 45,420 l (12,000 gallon). A mixer was mounted on top of one of the tanks to provide uniform mixing of the waste before application. Contents of the other tank were pumped to the mixed equipped tank prior to application.

Sludge Application

Sludges were applied to the plots with an applicator attached to a 750 l tank equipped with a 5 hp gasoline engine powered pump. The applicator were designed and constructed by University of Oklahoma personnel, consisted of a 2.7 m (9 ft) manifold with six spray nozzels equally spaced to assure uniform applications. A 1/2 hp motor drove the manifold along a 20 ft frame (Figure 4.4). One pass of the manifold applied sludge uniformly to the entire 6 m x 2.7 m (20 ft x 9 ft) plot. The amount of oil applied to each plot was controlled by the number of passes. Before each application the plots were tilled, and the applicator calibrated.

Figure 4.3. Partial view of land treatment facility.

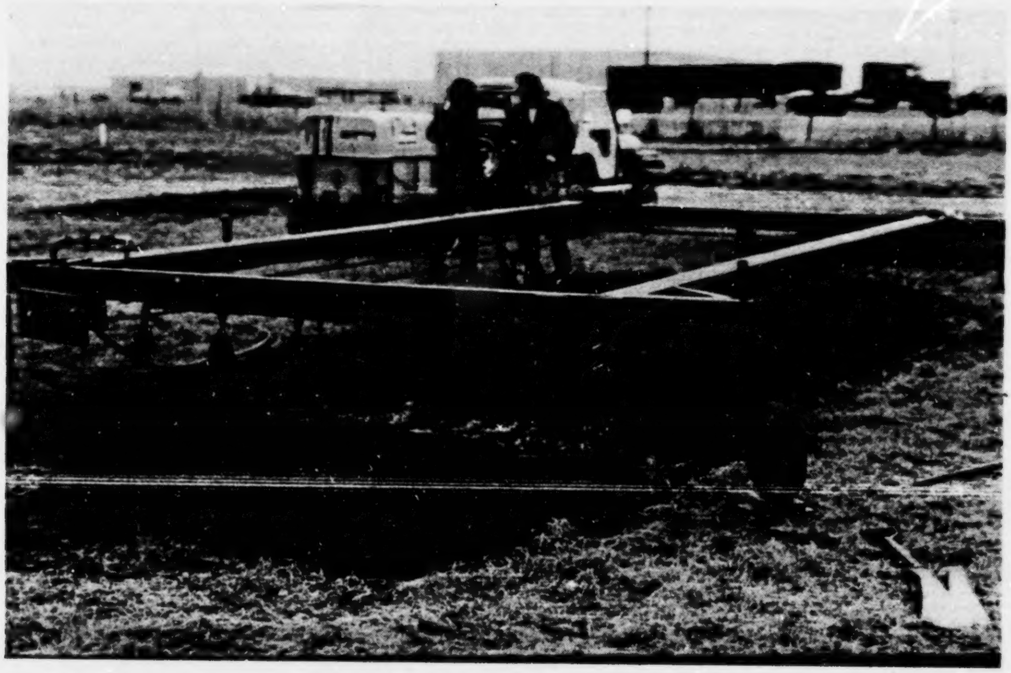


Figure 4.4. Sludge applicator.

Tilling was performed using a John Deere 850 tractor and a 1.5 m (5 ft) rototiller. After application the plots were immediately tilled twice to ensure uniform mixing of the oily sludge in the zone of incorporation. Design till zone depth was 30 cm (12 in).

Process Control Consideration

The objectives of this study were to determine the controlling factors for land treatment of refinery residues and to optimize these factors for design purposes. Factors widely identified as controlling the land treatment process for oily sludges are:

(1) Relative composition of the organic fraction of the sludge;
(2) Temperature;
(3) Water;
(4) Nutrients;
(5) pH; and
(6) Oxygen availability.

Although these factors are important and were monitored or controlled in this study, they were not the main factors emphasized. The primary factors were loading rates, loading frequencies and tilling.

For the purpose of this study, the first three factors mentioned above were monitored but not controlled. The relative concentration of various fractions of oil in the sludge was dictated by process conditions in the refinery. Temperature and water are climatic factors which were allowed to vary naturally. Although moisture conditions can be partially controlled by extensive drainage systems and by irrigation; the decision made by the researcher, supported by EPA personnel, was to operate the system under natural climatic and moisture conditions.

Nutrients and pH can be controlled to a large extent by the addition of fertilizers and lime. The soil pH is an important parameter for biodegradation, and also for immobilization on the heavy metals found in the sludge. Nutrients are required for the biological processes to proceed efficiently. Routine monitoring of pH and nitrate nitrogen was performed as discussed in the results section of this report. In addition, the concentration of chloride ion was monitored.

The availability of oxygen throughout the zone of incorporation is extremely important for bio-oxidation of the organic materials. Oxygen availability is a function of tilling, loading rates and moisture content. The oxygen was primarily controlled in this project by cultivation or tilling the zone of incorporation. Proper mixing and aeration of the soil in the zone of incorporation is an integral part of the land treatment process. The function of tilling is analagous to the function of aeration in an activated sludge wastewater treatment process; it provides mixing and aeration of the residue-laden soil.

A relatively large amount of information exists on the soil-water relationship as it impacts common agriculture practices such as field preparation, crop cultivation, erosion management, etc. In contrast, very little information is available regarding moisture relationships of soils to which oil sludges have been applied. In the land treatment of oily sludge, the complexity of soil-water relationships is increased by the addition of oil. In fact, the effects of various fractions of oil, oil-water emulsions, and other matrix interactions make thorough understanding of factors relevant to the soil tilling process very difficult. It was beyond the scope of this study to explore in-depth the complex relationships of oil, water, and soil in the zone of incorporation.

Experimental Design

The original experimental plan called for a 4 x 4 factorial design with oil loading rate and application frequency as the treatment parameters. Four values of loading rate and loading frequency were selected to cover the range of practical loading conditions. Replicates of each combination were to be used for increased statistical significance.

The first application to the plots occurred in August 1981. For this application the loading rates of oil were 3, 5, 9, and 13 percent (soil dry weight basis), with application frequencies of 1, 6, 12, and 18 applications per year. During the August 1981 application the high rate - low frequency plots could not be fully loaded, due to the constraint imposed by the field capacity of the soils. Even duplicate plots could not be loaded to the same level because of varying antecedent soil conditions. Thus, several plots only received a fraction of the nominal loading. It was intended to apply the total planned quantities within a few days to simulate a single loading of the plot.

However, immediately following the first application, heavy rains prevented further tilling, application, and sampling until January 1982.

Since the original plan could no longer be followed, a change was made in the nominal treatment loading rates and frequencies. Once again, several of the high rate - low frequency plots could not be fully loaded at the nominal rate. Although many attempts were made until November 1982 to maintain the schedule, the actual loading rates and frequencies did not correspond to the planned treatments. A third treatment schedule was then developed, and new plots added so that high rate - low frequency plots could be evaluated.

Weather conditions continued to plague the project, forcing application, tilling, and sampling as weather permitted. The amount of sludge and time of application was recorded for each plot.

A compilation of oil loadings (as percent of dry soil weight) given to each plot is presented in Table A.1, Appendix A. These tables give date of loading, elapsed time since the first sludge application, and the amount of oil applied as a percent of dry soil weight.

A comparison of total cumulative oil loadings for each plot is given in Table 4.4. Using total loading as a criterion for replicate comparison, only six total loadings were replicated. Of the six sets of total loading replicates only four sets of plots are actually true replicates which were loaded the same amounts on the same dates. The other plots, though applied with the same cumulative amount of oil, were not loaded on the same days and therefore, cannot be considered true replicates.

Tilling

One objective of this study was to evaluate the optimum tilling frequency. It was originally intended to perform an experiment using several plots which had received the same oil loading, with tilling frequency as the process variable and oil loss rate as the criteria for evaluation.

Following the initiation of the oil loading it became evident that wet field conditions precluded operation of the rototiller and tractor, thus, imposing a rigid tilling schedule without regard to field conditions and soil-oil-water relationships was neither practical nor desirable. When attempts were made to till plots

TABLE 4.4. TOTAL CUMULATIVE OIL LOADINGS - 1981, 1982

Plot No.	Total Loading % Oil (dwb) *
1	20.04
2	10.79
4	4.15
5	14.88
6	22.54
7	8.53
8	26.50
9	5.49
10	14.76
11	8.53
13	9.20
14	3.74
15	14.76
16	10.35
17	8.63
18	2.78
20	14.30
21	22.81
22	22.43
23	21.68
24	7.48
25	2.21
26	12.04
28	24.23
29	22.50
30	14.20
31	8.63
32	4.92
34	8.24
35	18.71
36	12.56
38	7.48

* dwb = soil dry weight basis

which were wet, it was difficult to control tilling depth and preserve plot boundary dimensions. Deepening the zone of incorporation and lateral enlargement of plots was to be avoided so that the computation of mass balances would not be influenced.

As discussed above, the research site was designed with an approximately 1 percent slope from west to east to allow surface run-off to flow overland to a retention pond. Though the surface drainage between plots was adequate, the test plots themselves were poorly drained. Tilling operations in the zone of incorporation increased the volume of pore space within the soil matrix. Thus, each plot behaved like a sponge surrounded by relatively impermeable undisturbed soil.

Water loss from the soil may be slowed by the presence of oil. Meyers and Huddleston (1979) suggested that oil addition increases the hydrophobic properties of agricultural soils. Whether persistence of excess soil moisture in test plots was the result of increased moisture holding capacity or the result of physical containment due to the physical configuration of the plots is not known.

During wet conditions, soil in the zone of incorporation had a 'pudding-like' consistency with a moisture content above and at time's above the liquid limit, above the field capacity. After a period of drying, the plots would appear dry and crusty on the surface; however, beneath this 2-4 cm crust, the plots remained wet. As a rule of thumb, if a stake could be easily inserted into the plot by hand, the plot was too wet to till.

Once the plots had dried sufficient for operation of the tilling equipment, they were tilled several times to speed the drying process. Tilling the soil in a plastic condition tended to form clumps of approximately 10 cm (4 in) diameter, and further tilling did not appreciably reduce this size.

The agglomerated clumps in the zone of incorporation created a condition of large void spaces within the tilled depth. The cohesion of the soil in these clumps increased dramatically upon further drying. Examination of cross-sections of these clumps revealed low macro-pore space volume, thus, oxygenation was occurring only at the outer surface. Tilling of the dried clumps did not significantly reduce their size but only rearranged them. In addition, resistance of the clumps to the shearing action of the rototiller made tilling to the required depth difficult.

Inclimate weather made it impossible to maintain the loading rates and frequencies established in the original design, and to till the plots as desired. Limited tilling hampered sampling efforts, leading to a somewhat irregular pattern of sampling. For most of the study, sampling dates closely corresponded to application dates. Zone of incorporation soil samples were typically obtained prior to each sludge application, with other types of samples such as deep cores obtained on a more infrequent basis. In some cases, plots were sampled more than once between applications, especially if oil was applied on a low frequency basis.

In an effort to improve the precision and accuracy of oil content measurements, sampling and analytical methodology constantly evolved throughout the first year of the project. The sample preparation and analysis methods developed during this period are located in Section 5.

SECTION 5

PROCEDURES

SAMPLING METHODS

Soil Sampling

Sampling is one of the most important steps in data collection and analysis. A representative sample must be obtained in order to obtain consistent and meaningful results. Studies were performed to establish a sampling method.

The initial sampling method consisted of a single sample from each plot using a 2.54 cm (1 in) Shelby tube. Analysis of the data showed that based upon the amount of oil applied to each plot effective oil recoveries and consistent results were not obtained. The second method consisted of obtaining five samples from each plot; each sample consisting of a composite of twenty 2.54 cm (1 in) in diameter, 0.3 m (1 ft) long Shelby tube cores. The high variability resulting from this method was attributed to the diameter of the Shelby tube being less than the maximum diameter of a significant portion of the agglomerated particles.

In order to reduce the variability, two other methods of sampling were studied. One consisted of using a 8.9 cm (3.5 in) diameter sampling tube and obtaining three cores randomly across the site per composite sample and taking three samples per plot. The second method consisted of using a 4.8 cm (1.9 in) sampling tube, obtaining 10 cores randomly per composite sample and 3 samples per plot. Statistically, in analyzing the data obtained from these two sampling methods, the method using the 4.8 cm (1.9 in) sampler gave less variation in the analyses than the 8.9 cm (3.5 in) diameter sampler. Hence, the method using the 4.8 cm (1.9 in) sampler was selected. Table 5.1 shows the variations in the sampling methods.

Ground Water Sampling

Samples from the four monitoring wells were obtained using a 5 cm (2 in) diameter Kemmerer sampler. The sampler consisted of a 0.94 m (3 ft) long stainless steel cylinder with Teflon caps on both ends suspended by a 61 m (200 ft) nylon cord. Samples were collected in 500 ml glass bottles prewashed with soap solution and organic free water as outlined by EPA procedures.

Soil Moisture Sampling

The soil water passing through the unsaturated zone beneath the zone of incorporation was also sampled. Sampling of the soil pore water was accomplished by installing soil moisture samplers (lysimeters) at a depth of approximately 1.2 m (4 ft) at the site. The sampler used was Model 1920, sold by Soil Moisture Incorporation of California. It was installed according to the following procedure.

A 10 cm (4 in) hole was drilled to the required depth, and thoroughly cleaned out, making sure that the hole was not contaminated with soil from the zone of incorporation. The bottom of the hole was tamped, and the sampler was seated in 300 mesh-silica sand, so that the ceramic cup of the sampler was completely covered. Parent soil (15 cm) was placed back in the hole, and tightly tamped. A layer of dry bentonite clay was then placed in

TABLE 5.1. STATISTICAL ANALYSIS FOR CHOICE OF SAMPLER

Sample	% Oil	Mean	Deviation	SS	D.F.
Medium Sampler (1 7/8" dia.)					
6-1-1	8.4834		0.00187		
6-1-2	8.4250	8.4815	-0.05653	0.006188	2
6-1-3	8.5362	(0.2320)	0.05467		
SS = 0.245244		MSS = 0.122622			
6-2-1	8.3975		-0.02283		
6-2-2	8.2848	8.4203	-0.13553	0.043971	2
6-2-3	8.5787	(0.1708)	0.15337		
6-3-1	7.9491		0.10243		
6-3-2	7.8668	7.8467	0.02013	0.025921	2
6-3-3	7.7241	(-0.4028)	-0.12257		
		8.2495		ESS 0.076030	6
0.012680 EMS analysis					
Large Sampler (3" dia.)					
6-1-1	6.9641		-0.05777		
6-1-2	6.3943	7.0219	-0.62757	0.866857	2
6-1-3	7.7072		0.68533		
SS = 0.103262		MSS = 0.103262			
6-2-1	8.9178		0.40103		
6-2-2	8.0809	8.5168	-0.43587	0.352021	2
6-2-3	8.5516	(0.2272)	0.03453		
6-3-1	8.1635		0.10120		
6-3-2	8.3353	8.0623	0.27300	0.224796	2
6-3-3	7.6881	(-0.2273)			
		7.8670		ESS 1.443676	6
0.240613 EMS analysis					

the hole followed by more parent soil. The hole was filled to about 20 cm (8 in) from the top with parent soil, which was added in small amounts and tightly tamped. Another layer of 5-8 cm (2-3 in) of dry bentonite clay was then added and the hole filled with soil. Figure 5.1 is a diagram of the mode of installation.

The principle involved in the operation of a lysimeter is that a vacuum is applied to the suction side of the tubing as shown in Figure 5.2. Vacuum is displaced by moisture entering in through the porous cup at the bottom of the lysimeter tube. Initially the water saturates the pores of the ceramic cup and then water flows into the cup due to the vacuum applied. The sample is collected from the ceramic cup by applying a positive pressure thereby displacing the water.

Sludge Sampling

Sludge samples were obtained from the storage tanks by lowering a 500 ml sampling bottle into the tank and retrieving a sample. Prior to sampling, the mixer was turned on for approximately 12 hours to insure complete mixing of the tank contents.

Air Sampling for Volatile Organics

Methodology for sampling volatile organics from land treatment sites was not available; therefore, the first quarter of this project was devoted to developing methodology for reliably sampling and accurately analyzing volatile compounds being emitted to the atmosphere from land treatment of petroleum sludge. Laboratory and field studies were performed to determine the effects of loading rates and frequencies, air and soil temperature, soil moisture content, relative humidity and sludge volatility on the magnitude and rates of volatile organic losses.

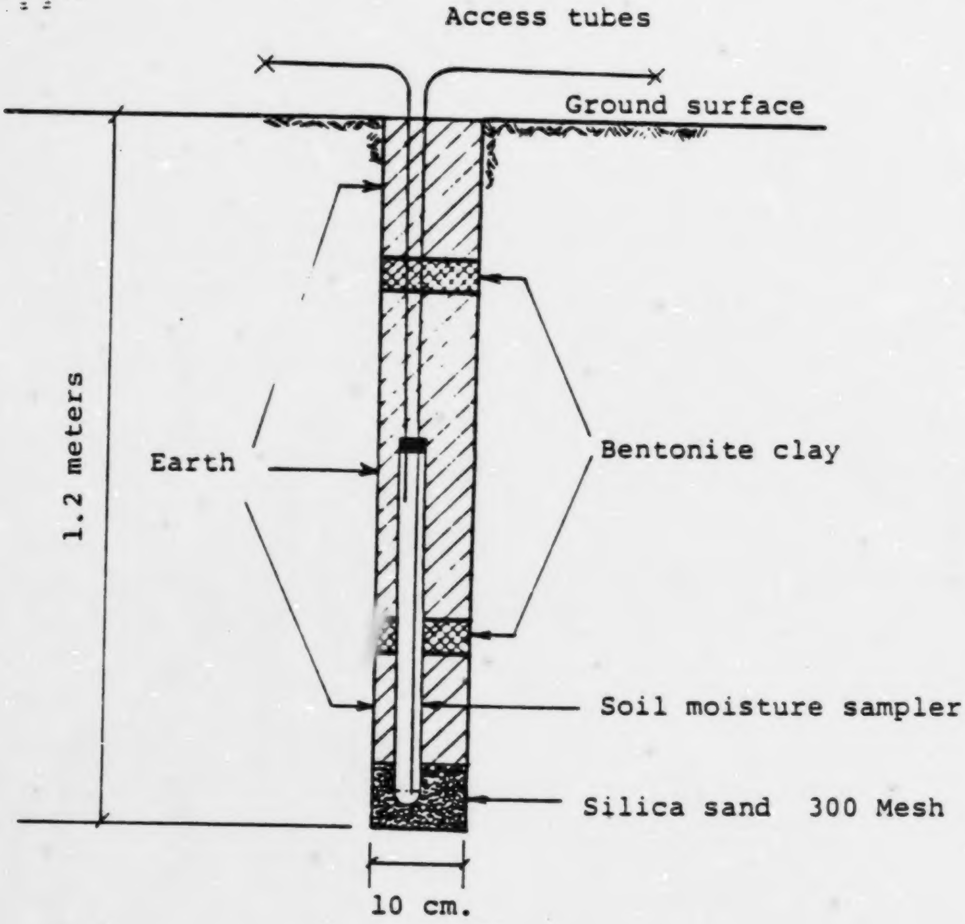

Access tubes
Ground surface
1.2 meters
Earth
Bentonite clay
Soil moisture sampler
Silica sand 300 Mesh
10 cm.

Figure 5.1. Method of installation of soil pore water sampler.

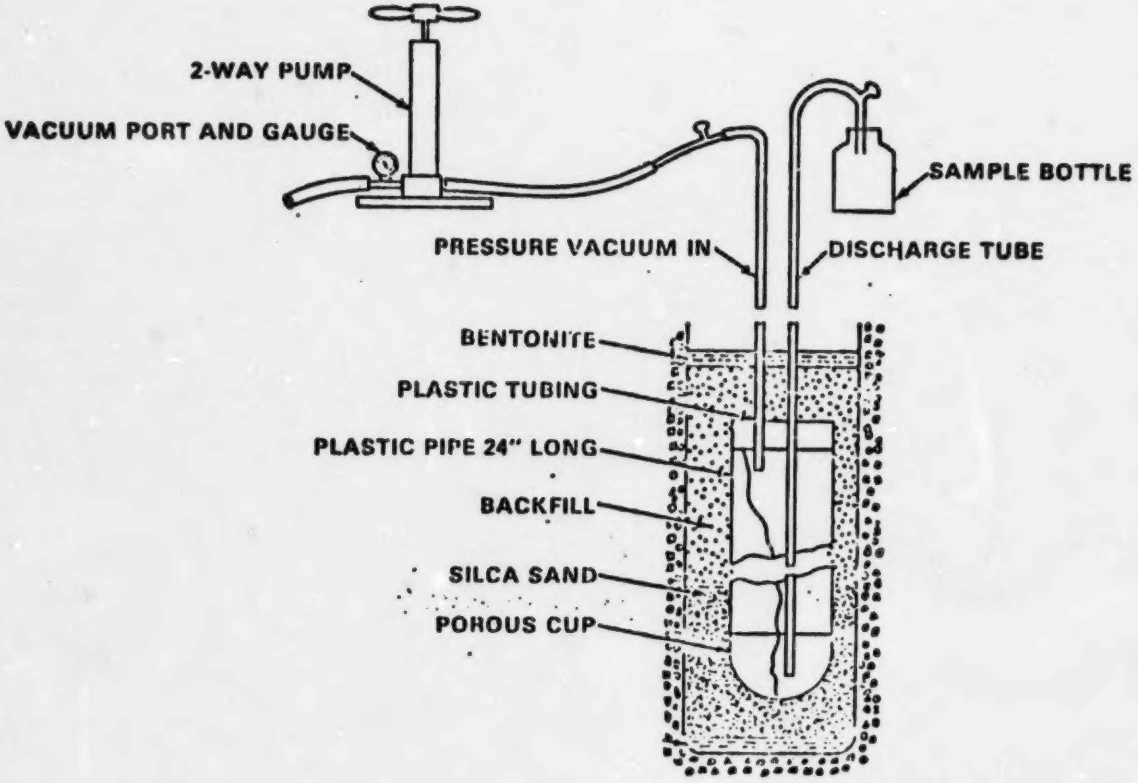

2-WAY PUMP
VACUUM PORT AND GAUGE
SAMPLE BOTTLE
PRESSURE VACUUM IN
DISCHARGE TUBE
BENTONITE
PLASTIC TUBING
PLASTIC PIPE 24" LONG
BACKFILL
SILCA SAND
POROUS CUP

Figure 5.2. Vacuum soil moisture sampler.

ANALYTICAL ANALYSIS

Simulation Equipment for Air Sampling

A simple system for the measurement of the rate of emission of volatile hydrocarbons resulting from the land treatment operation of petroleum oily sludge was designed and constructed. Flexibility, simplicity, reliability, portability and durability were features sought in the design of the monitoring and collection system. Figures 5.3 and 5.4 depict the simulation apparatus used in the field and laboratory, respectively. Figure 5.5 shows the physical arrangement of the apparatus in the field.

This design incorporated an insulated, rectangular, open bottom chamber fabricated from aluminum with a length of 41 cm (11 in), a width of 14.6 cm (5.7 in) and a height of 29 cm (11.4 in). It was insulated with 4 cm (1.6 in) of styrofoam. The bottom of the chamber circumscribed an area of 0.07 m^2 (0.78 ft^2). The following accessories were provided:

1. A small variable speed AC fan was installed on the top of the chamber to mix the air within the chamber.
2. Two dial thermometers were inserted through ports to record air and soil temperature inside the chamber.
3. A dew point hygrometer was used to measure vapor pressure and relative humidity inside the chamber.
4. A port through which breathing quality compressed air was provided to transport pollutants from the sampling chamber to the hydrocarbon detector and columns packed with appropriate adsorbents. Air flow rate was controlled with a regulator equipped with a flow meter.

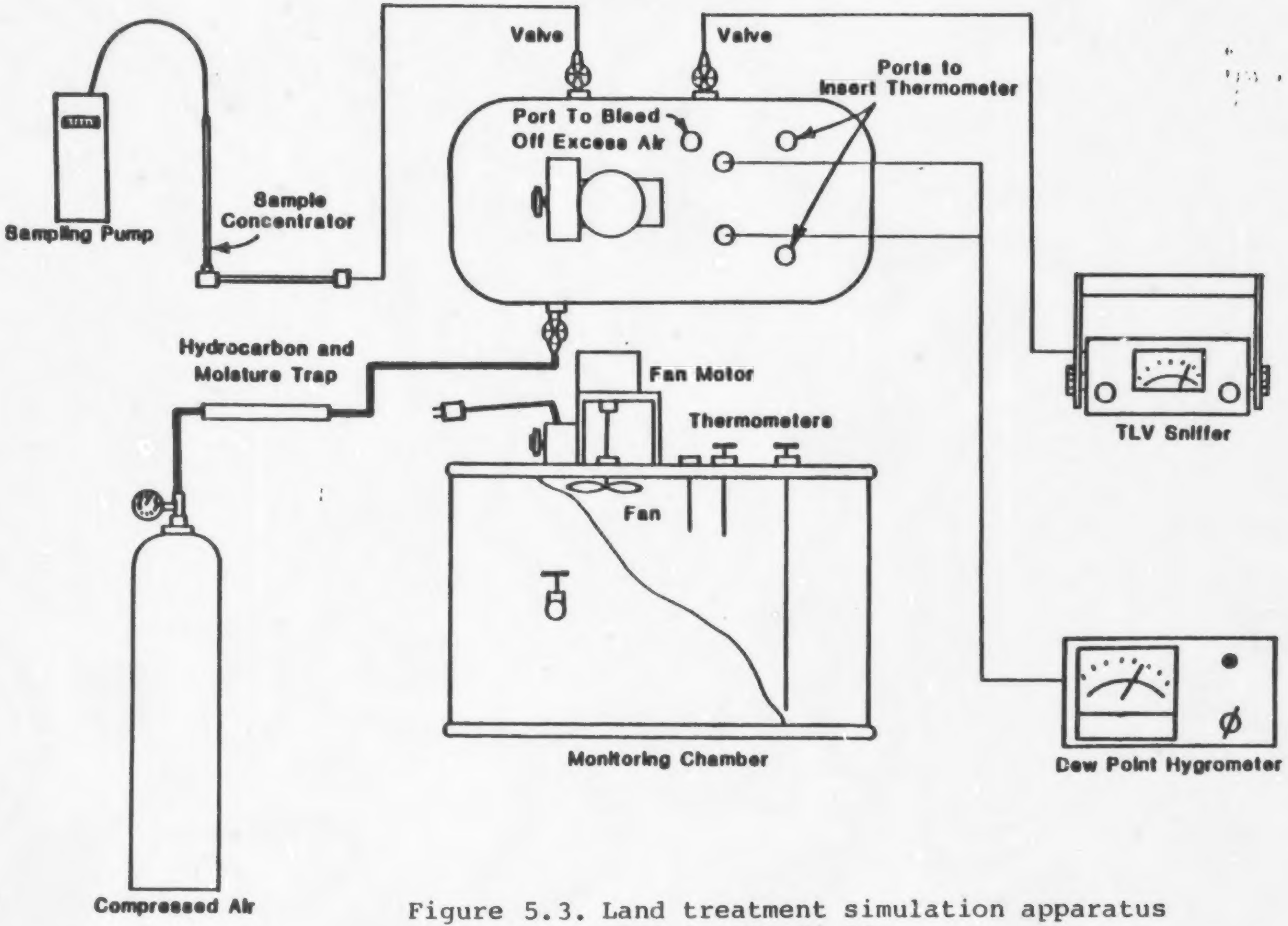

Valve
Valve
Ports to
Insert Thermometer
Port To Bleed
Off Excess Air
Sampling Pump
Sample
Concentrator
Hydrocarbon and
Moisture Trap
Fan Motor
Thermometers
Fan
TLV Sniffer
Monitoring Chamber
Dew Point Hygrometer
Compressed Air

Figure 5.3. Land treatment simulation apparatus used in the field.

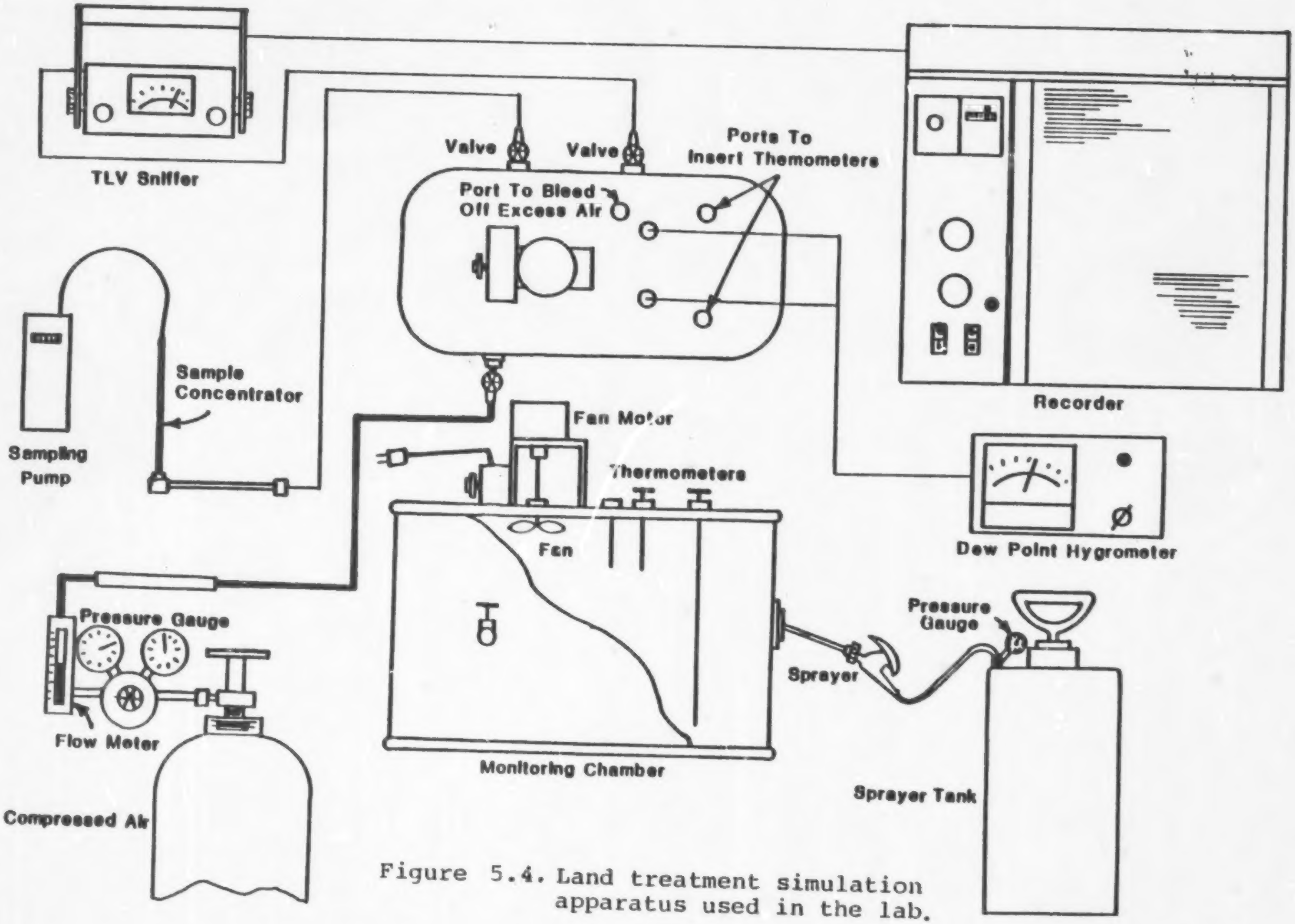

TLV Sniffer
Valve
Valve
Ports To
Insert Themometers
Port To Bleed
Off Excess Air
Recorder
Sampling
Pump
Sample
Concentrator
Fan Motor
Thermometers
Fan
Dew Point Hygrometer
Pressure Gauge
Flow Meter
Compressed Air
Monitoring Chamber
Pressure
Gauge
Sprayer
Sprayer Tank

Figure 5.4. Land treatment simulation apparatus used in the lab.

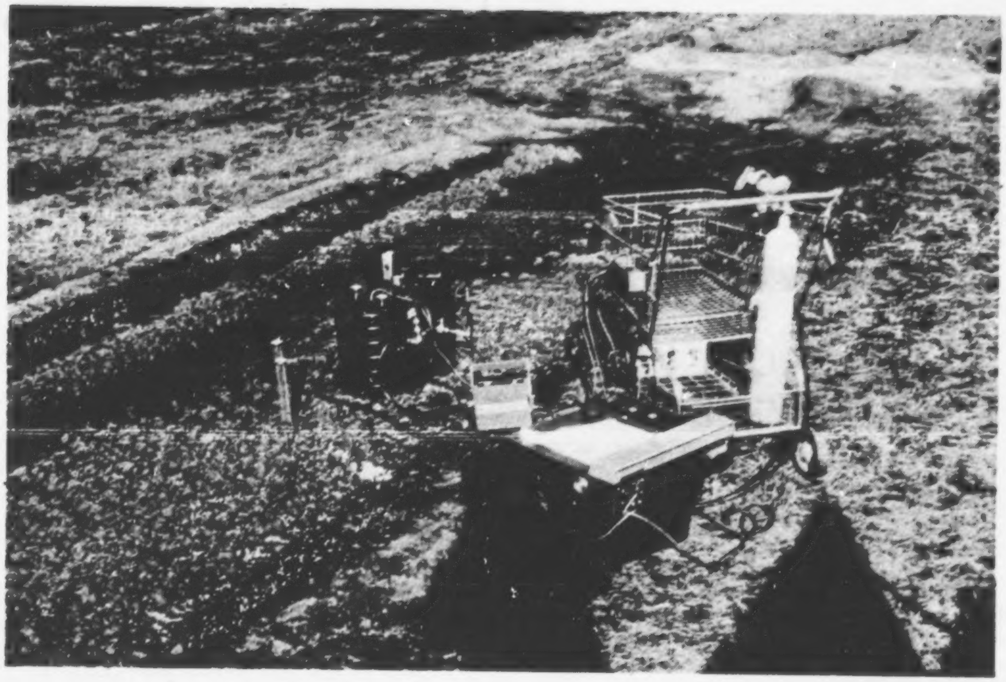


Figure 5.5. Air monitoring equipment set up in the field.

5. Ports were provided on the opposite end of the chamber from the inlet port, to monitor total volatile hydrocarbon by a Bacharach Instrument Co. TLV Sniffer and to concentrate volatile compounds on an appropriate adsorbent material.
6. A sprayer consisting of a two-gallon, polished stainless steel tank, with removable syphon tube, hose adaptor and discharge unit was attached to a fan pattern nozzle inside the chamber to distribute the sludge evenly over the soil surface.
7. The inside of the chamber was coated with epoxy paint to eliminate contamination from the aluminum.
8. To insure a good seal between the chamber and the soil surface, an aluminum band 3.8 cm (1.5 in) in depth was extended from the bottom edge of the box and embedded in the soil.

Preparation of Equipment for Sampling

The TLV Sniffer, used for monitoring total volatile hydrocarbons, was calibrated with hexane; calibration was checked with known concentrations of hexane before and after each run.

A MDA scientific accuhaler model 808 personal sampling pump, used for collecting volatiles in adsorbent tubes, was also calibrated before and after sampling using a soap bubble flow meter. Flow rate through the trap was 30 to 31 ml/min.

The hygrometer probes were dried in a 60-80°C (140-180°F) oven for about 1/2 hour to remove excess moisture before using.

Field Sampling Protocol and Procedure

After the measurement methodology was developed and equipment was tested and calibrated in the laboratory, field studies were conducted at the research site. Oil was applied to the soil surface at five loading rates, with varying frequencies.

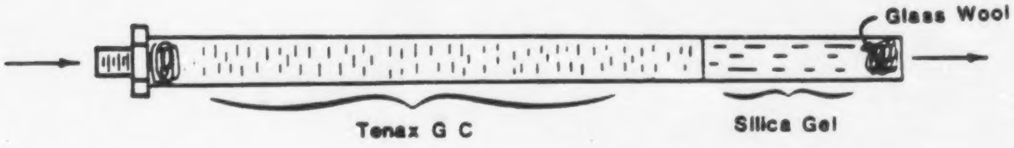
The procedure for using the chamber involved placing it over the plot and inserting it into the soil to a depth of 3.8 cm (1.5 in). Meanwhile, the air control valve was opened to maintain the desired air flow rate and the head-space fan was turned on. To allow equilibration, the dew point hygrometer was turned on at least 10 minutes before sampling. The hygrometer probes were inserted into the chamber through two sealable ports on the top surface of the chamber.

Soil and air temperatures were determined by dial thermometers (range -40 to 71°C). The temperature of the air within the chamber was measured at 6.4 cm (2.5 in) above ground level. The temperature of air outside the chamber was also measured at the same height. The temperatures of soil inside and outside the chamber were measured at a depth of 5 cm (2 in) below ground level. Samples were taken using the TLV Sniffer and solid sorbent tubes.

The Sniffer was purged for at least 10 minutes prior to sampling. It was then zeroed with ambient air prior to sampling. The Sniffer probe was connected to the brass quick connect (Figures 5.2 and 5.3) valve in one side of the chamber. The total volatile hydrocarbon concentration in the air leaving the chamber was then monitored with the Sniffer until equilibrium concentration was reached. Samples were collected according to the predetermined sampling schedule. The sampling schedule was adjusted to take into consideration abnormalities in the field. The resulting sampling schedule was determined by the concentration vs time curve which was the product of many experiments.

To determine the identity and relative quantity of organic pollutants, sampling was also performed by drawing exiting air through a 0.64 cm (2.5 in) (outside diameter) stainless steel trap packed with 7.6 cm (3 in) of Tenax-GC (60/80) and 2.54 cm (1 in) of silica gel (100/200). Figure 5.6 shows the sampling cartridge.

Tenax-GC, a typical sorbent for collecting volatile compounds at room temperature, is a porous polymer that is based on 2,6-diphenyl-p-phenylene oxide. However, many of the lighter organic compounds are not adequately retained at room temperature by Tenax-GC (Bertsch et al., 1974). By using the cryogenic method, in addition to increasing the efficiency of collecting low molecular weight hydrocarbons (C_{2}-C_{6}) (Singh, 1980; Bertsch et al., 1980; Seifert and Ullrich, 1978; Altschuller, et al., 1971; Hodren et al., 1979), the oxidation or polymerization of constituents is minimized (Singh, 1980). Nevertheless, cryogenic trapping was dismissed due to difficulty of using this system in the field.



Dimensions: 4 $\frac{2}{5}$ in. by .25in. O.D. Stainless Steel Tube

Figure 5.6. Sample concentrator.

Pellizzari (1974, 1975) developed an analytical technique to determine the collection efficiency of many sorbents, including Tenax-GC, during the concentration of hazardous vapors from a moving air stream. He reported that Tenax-GC was greater than 90 percent efficient in trapping hazardous vapors.

Silica gel exhibits a great selectivity among atmospheric gaseous and vaporous constituents. It readily adsorbs compounds with hydroxyl groups and with many of the more common halogenated hydrocarbons (Thain, 1980; Altschuller et al., 1962). Organic compounds with a minimum of three atoms would be trapped on silica gel. Silica gel adsorbs water more than any other substance; therefore, under conditions of high humidity, the efficiency of adsorbing other compounds is much reduced (Thain, 1980; Buonicore and Theodore, 1975; EPA, 1976).

The addition of a small amount of silica gel in front of Tenax-GC served to protect the Tenax-GC from the moisture without altering the efficiency and to trap organic compounds that were not trapped by Tenax-GC.

To prepare the traps, the tubing was first cleaned using a soap solution and then distilled water, and was subsequently rinsed with methanol and oven dried. A glass wool plug was inserted, and the sorbents were added, followed by slight tapping an another glass wool plug to hold the sorbent material.

After trap preparation and before sampling, a clean trap was analyzed as a blank by Gas Chromatograph-Flame Ionization Detector (GC-FID). Analyses of two traps indicated some quantities of methylene chloride. Investigation revealed that the methylene chloride was a contaminant from the laboratory used for oil content analysis. Subsequently, traps were transferred to and from the field in an ice chest at 4°C to help avoid contamination to refrigerate sample.

To start sampling, a quick connect stainless steel valve was used to connect the trap to the chamber. The use of quick connect valve facilitated sampling and storage operations. All fittings used were stainless steel or brass. Two cartridges in series were used periodically to check for breakthrough. Volatiles were collected using MDA Accuhaler 808 personal sampling pump.

The length of time of sampling varied depending on the concentration of the volatiles: after application, with high concentration of volatiles, 5 minutes; after tilling, with moderate concentration, 10 minutes; and before application and tilling, 20 minutes. The collected samples, which were sealed, labeled and refrigerated in the field, were analyzed in the laboratory within a week. Weather permitting, samples were taken before and immediately after application, before and after tilling, as well as every other week until the next application.

Laboratory Evaluations

Field measurements of volatile hydrocarbons were complemented by conducting limited exploratory measurements in the laboratory in a temperature and humidity controlled environmental chamber. Volatilization rates of the waste were studied at three different temperatures. In addition, for each temperature range, the application rate was varied. In these tests the soil moisture content and relative humidity were held constant. Other tests were performed with varying soil moistures at fixed temperatures and loading rates. The purpose of this study was to determine the effects of soil temperature, loading rate, soil moisture content, and relative humidity on the rate of emission of volatiles. Sludge volatility was kept relatively constant for all experimental runs by applying one API separator sludge from the same batch. Prior to each application, the volatility of the sludge was determined to detect any changes. (Table 5.2 presents the experimental conditions for the laboratory study.)

For each temperature range four rectangular wooden boxes 33 x 31 x 25 cm (13.0 x 12.2 x 9.8 in) filled to a depth of 20 cm (8 in) with soil from the field research site were placed in the environmental chamber. The desired air temperature was set and the monitoring chamber was placed over the soil in one of the boxes.

The appropriate volume of sludge was poured into the sprayer tank, connected to the monitoring chamber, and the tank was pressurized to a maximum of 30 psi. When all of the desired test conditions were stabilized, the background hydrocarbon concentration was recorded and the sludge applied evenly over the surface. During the application and for one hour afterward, the atmosphere of head space was continuously monitored using the TLV Sniffer connected to a chart recorder. After the sludge was applied and volatiles were monitored, a small garden hoe was used to completely mix the soil to a depth of 20 cm (8 in).

Each series of experiments was performed over a seven day period. Sampling and monitoring took place before and during application, immediately after application, before and immediately after tilling, at two hour intervals throughout the first day of application, and daily for the next two days. The soil and sludge mixture was tilled on the third and fifth days after application. In all, 18 samples were taken with the TLV Sniffer in each run, and 10 samples were taken for GC analyses, using adsorbent tubes for each temperature and loading rate range.

Oxygen Monitoring

Oxygen monitoring was carried out in the zone of in-

TABLE 5.2. EXPERIMENTAL CONDITIONS FOR LABORATORY STUDY

Run. No.	Loading Rate (% oil in soil-dry wt.)	Soil Temp. °F	Soil Mois. Cont. (wt %)	Relative Humidity (%)	Air Flow Thru the Box (l/min)
1	3	35	12	52	3.5
2	6	35	12	52	3.5
3	10	35	12	52	3.5
4	3	60	12	52	3.5
5	6	60	12	52	3.5
6	10	60	12	52	3.5
7	3	85	12	52	3.5
8	6	85	12	52	3.5
9	10	85	12	52	3.5
10	6	60	23	52	3.5
11	10	60	23	52	3.5
12	6	60	12	70	3.5
13	10	60	12	70	3.5

corporation using a Beckman model D2 paramagnetic oxygen analyzer. This instrument provides a direct readout of the oxygen concentration as a percentage of the total air sample. The monitor utilizes the paramagnetic properties of oxygen. Air samples drawn into the monitor are subjected to a magnetic field, which exerts an attractive force on the sample which is proportional to the amount of oxygen present in the sample. This attractive force is translated into a readout of the percentage of oxygen in the sample.

The sample is drawn into the analyzer via a tube inserted to the depth at which the soil atmosphere is to be monitored. The sample was drawn into the analyzer by manual operation of a small aspirator bulb.

ANALYTICAL METHODS

Oil Content Analyses

Three different procedures were used in the determination of oil content. The procedure used with a specific sample depended on the nature of the sample. The discussion of procedures is divided into two sections, sample preparation and analysis.

Sample Preparation

Sample preparation techniques were dependent on the sample matrix and the moisture content of the sample. During the research project, an extensive study of sample preparation techniques for different types of soil samples were made. Samples can be classified into four different classes:

1. Friable samples (moisture content less than 18 percent for soil used in this study).
2. Wet samples with moisture content approaching the plastic limit (18 percent).

3. Sludge samples
4. Liquid samples

Class 1--

The samples obtained from the field were first mixed and quartered to obtain approximately 500 gms of soil. The sample was then blended until it could pass through a No. 10 sieve. Once the entire sample had been blended and passed through the No. 10 sieve, the sample was quartered until the required sample size was obtained.

Class 2--

These samples were difficult to work because of the inconsistency in the sample and the high moisture content. The samples were mixed using a mortar mixer, Model C-100 with intermittent scraping of the soil from the sides and the blades until a uniform sample consistency was obtained. The sample was chopped until the particle sizes were small compared to the overall samples. A flat 2.1 cm (1 in) stainless steel blade spatula was used to chop the sample. It was then quartered several times until the required sample size was obtained. The sample was then mixed with a drying agent magnesium sulfate ($Mg SO_4$) and pulverized in a mortar and pestle.

Classes 3 and 4--

Samples were thoroughly mixed and an aliquot of the sample was taken for analyses.

Analysis

There are three basic methods for oil content analyses as mentioned in the "Standard Methods for the Examination of Water and Wastewater", 15th edition and the "Test Methods for Evaluating Solid Waste Physical/ Chemical Methods", July 1982 EPA SW846, 2nd ed. The three methods are; 1) gravimetric extraction, 2) infrared spectrophotometry, and 3) Soxhlet extraction. The method used in this study was the Soxhlet extraction method.

Two factors which influence the Soxhlet extraction process are the solvent used and the method of evaporation of the solvent. The different types of solvent media used for evaluation of the extractions process were:

1) 15 percent diethyl ether and 85 percent freon
2) 15 percent diethyl ether and 85 percent methylene chloride
3) freon
4) methylene chloride

The method of evaporation was varied from that followed by Standard Methods wherein the solvent was evaporated at 70°C. This procedure resulted in the loss of volatile compounds in the sample matrix. In order to avoid loss of volatiles, samples were evaporated on a steam bath until a volume of approximately 15 ml of solvent was left in the evaporating flask and then transferred to a preweighed aluminum weighing dish. The sample further was evaporated at room temperature in a hood, overnight. An inert gas nitrogen (N_2) was passed over the sample to drive off any remaining solvent before weighing (McGill and Rowell, 1980).

Several methods of extraction were evaluated using different solvents. The methods were:

(1) Freon Extraction - Method 503-C "Standard Methods for the Examination of Water and Wastewater".
(2) Soxhlet Extraction with Methylene Chloride - McGill and Rowell (1980).
(3) Soxhlet Extract with Freon - modification of method of McGill and Rowell.

Results of this study, Table 5.3, show the best recovery is the new method using methylene chloride as the solvent. The loading rate for this analysis was 10 percent oil of dry weight soil.

TABLE 5.3. COMPARISON OF OIL CONTENT ANALYSIS METHODS

#	Solvent and Method of Analysis	% of Oil Recovered on a Dry Wt. Soil Basis
1	Freon, Standard Method	8.6
2	Methylene Chloride, (McGill and Rowell)	9.9
3	Freon, New Method (McGill and Rowell)	9.4

Fractionation Analysis

This study involves the separation of petroleum residues into four fractions: asphaltenes, saturates, aromatics and polar compounds. Polar compounds are also referred to as resins.

Asphaltenes are defined as pentane insolubles that can be separated from a solution of oil in n-pentane and may include insoluble resinous bitumens produced by the oxidation of oil. Polar compounds are materials retained on adsorbent clay after percolation of the sample in a pentane eluent. Aromatics are materials that on percolation, passes through a column of adsorbent clay in a pentane eluent, but adsorbs on silica gel. Saturates are materials that on percolation in a n-pentane eluent are not adsorbed on either the clay or silica gel. The method used for this separation is the ASTM D2007-73.

Metal Analysis

Heavy metal analyses were carried out on sludges, site soil, soil/oil matrix, and soil moisture samples.

The sludges and soil samples were analyzed using a digestion procedure obtained from the Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma. In this procedure, between 0.2 and 1 gm of sample was accurately weighed in an acid-washed beaker, 10 ml of concentrated nitric acid added to the beaker, and the mixture evaporated just to dryness. Ten more ml of acid were then added to the beaker, and the beaker was covered and allowed to reflux gently for a minimum of 2 hours. When ashing of the sample was complete, indicated by the absence of vigorous reaction, the beaker was cooled, 1 ml of 30 percent hydrogen peroxide (H_2O_2) was added and the digestion continued. Additional 1 ml portions of H_2O_2 were added up to a maximum of 10 ml, until digestion was complete. This stage was denoted by no further changes in the color of the sample. The cover was then removed from the beaker, and the sample evaporated until just dry. Three ml of nitric acid were then added, the beaker heated to solubilize the residue, and 25 ml of water were added. The beaker was then covered, and the contents allowed to digest for 1 hour. The sample was then transferred to a 100 ml volumetric flask, diluted to volume, and analyzed by Atomic Absorption Spectrophotometry.

Aqueous samples were prepared for analysis using methods 3010 or 3020 from "Test Methods for Evaluating Solid Waste Physical/Chemical Methods" July 1982, EPA SW-846, 2nd ed., published by the Environmental Protection Agency.

All samples were analyzed on a Instrumentation Laboratory (IL) Model 551 Atomic Absorption Spectrophotometer, equipped with a Model 655 furnace and a model 254 fastact.

Chloride Analysis

The method used for chloride analysis of soils was taken from "Methods of Soil Analysis" published by the American Agronomy Society (Black et al., 1965). Both 1:5 and 1:1 ratios of soil to water were used. The chloride ion concentration in the soil pore water samples was determined using method 325.3 - titritmetric determination with mercuric nitrate - taken from the EPA manual "Methods for Chemical Analysis of Water and Wastes".

pH Determination

The pH determination for soils was done according to the procedure outlines in Methods of Soil Analysis (Black et al., 1965).

The soil sample was diluted 1:1 with water and mixed for 30 minutes. The mixture was allowed to stand for one hour to settle, and then the pH was determined using an Orion Model 401 pH meter with an Orion Model 91-02 electrode.

Nitrate

Soil nitrate determinations were carried out using the phenoldisulfonic acid method described in Part 2 of "Methods of Soil Analysis" published by the American Agronomy Society (Black et al., 1965). This procedure involves the development of a yellow color with phenoldisulfonic acid by the nitrate ion in an aqueous extract of the soil.

Priority Pollutant Analysis

The soil samples were extracted for priority pollutant analysis by using a combination of Methods 3540 and 3530 in the EPA Manual, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods" July 1982, EPA

SW-846, 2nd ed." In the first part of the procedure, the solid sample was subjected to Soxhlet extraction using dichloromethane, as described in Method 3540. The extract from this procedure was concentrated to about 2.5 ml, and 0.5 ml removed for analysis for volatiles. The remainder was then extracted by Method 3530, yielding base/neutral and phenolics fractions.

The three fractions obtained in the extraction stage were then analyzed by a GC/MS system. The system used was a Hewlett-Packard 5985A Mass Spectrometer, with a HP 5740 Gas Chromatograph and associated data system. Two different columns were used to analyze the three fractions. The base/neutrals and phenolics were analyzed on a DB-5, 30 meter, fused silica capillary column, and the volatiles were determined on a Carbopack C (60-80 mesh) coated with 0.2 percent carbowax 1500. The conditions under which the various fractions were run are given in Table 5.4.

TABLE 5.4. GC CONDITIONS FOR PRIORITY POLLUTANT ANALYSIS

	Volatiles	Base-Neutrals	Phenolics
Initial temp.	60°C	50°C	60°C
Initial hold time	3 min.	1 min.	1 min.
Ramp rate 1 (time in min.)	8°/min.	30°/min.(2)	30°/min.(2)
Ramp rate 2	-	8°/min.	8°/min.
Final temp.	160°C	300°C	270°C
Detector temp.	200°C	200°C	200°C
Injection temp.	175°C	250°C	200°C
Run time	25 min.	40 min.	20 min.

Carrier gas - Helium
Flow rate - 14 ml/min. for capillary column
25 ml/min. packed column

Standards were run at the start of each day's analysis, and identified from the mass spectrum of each peak obtained in the chromatogram. The unknown samples were run and the resulting data stored on a computer disk. Once all the samples were run, a standard file library of all the standards was created using a computer program written for identification and quantification called the IQ program. Each fraction - volatiles, base-neutrals and phenolics - had its own file. A data file was set up for the sample fractions, and matched against the files for the standards. The resulting printout was then analyzed for matches between the standards and unknown samples, and the concentrations of the compounds identified in the samples were calculated using response factors for the standards.

Air (Volatile Organics)

The collected samples were analyzed in the laboratory within a week by Hewlett-Packard (HP) Model 7675 purge and trap system and HP Model 5880A Gas Chromatograph (GC) equipped with Flame Ionization Detector (FID). A 0.32 cm (0.13 in) stainless steel column, packed with carbopack B/1 percent SP-1000 was used to separate the hydrocarbon compounds thermally desorbed from the sampling cartridge. Recovery of trapped vapors was accomplished using thermal desorption which allowed for direct introduction of the total sample into the GC column. Limited Gas Chromatography-Mass Spectrometry (GC-MS) analysis was also performed in the EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma for quality control.

The identity of volatile compounds was based on retention times of standard compounds and confirmed from subsequent GC analyses. Relative concentrations of compounds were determined using the Internal Standard (ISTD)

Calibration Method. Absolute quantities could not be given, since it was not known for all samples whether breakthrough has occurred from the sorbent trap. First, 1,4-dichlorobutane was used as an internal standard. However, with the last batch of sludge one compound co-eluted with 1,4-dichlorobutane, and they could not be separated by changing temperature programming nor even by using a capillary column. Therefore, after trying many compounds, methylene chloride was chosen to be used as an internal standard.

Since petroleum sludge contains a complex mixture of organic compounds, chromatographic separation of such compounds was a difficult task. Three different GC columns, including 60/80 carbopack C/.2 percent carbowax 1500, 10 percent SP-2100 on 100/120 suplecoport and 60/80 carbopack B/1 percent SP-1000, were examined at different conditions. It was found that 60/80 carbopack B/1 percent SP-1000 gave the best resolution. Nevertheless, peaks frequently overlapped, and it was difficult to identify and quantify all the unknown compounds. Thus, it was essential to reduce the number of organic compounds to be quantified. Of the volatile hydrocarbons identified, only fifteen were quantified. Table 5.5 presents these target compounds along with their retention times.

A calibration mixture of the fifteen compounds which were quantified (Table 5.5) was prepared every week. The purge and trap and GC were tested every day before the analysis of samples. The clean trap was then easily changed to the sample trap in the purge and trap system. A leak test was performed to confirm that all fittings were tight. Internal standard was first purged into the sample trap in a known concentrations. Nitrogen gas was used as a purge gas. Purge flow was maintained at 50

TABLE 5.5. POLLUTANTS IDENTIFIED AND QUANTIFIED IN AIR SAMPLES ALONG WITH THEIR RETENTION

Chromatographic Peak Number	Compound	Retention Time (min)
*1	Propanol	8.71
2	Methylene Chloride (IS)	9.30
*3	2-Propanone	9.56
4	Cyclopentane	13.47
*5	2-Butanone	18.05
6	Pentane	19.58
7	Cyclohexane	21.06
8	Methylcyclopentane	22.36
9	Benzene	26.84
10	Methylcyclohexane	29.84
*11	2,4-Dimethylpentane	31.46
12	Hexane	32.95
13	3-Methylhexane	35.58
14	1,4-Dichlorobutane (IS)	37.23
15	2,3,4-Trimethylpentane	38.995
16	2,5-Dimethylhexane	42.76
17	3-Methylheptane	44.65
18	2,2,5-Trimethylhexane	46.67
19	1,4-Dimethylbenzene	57.12
*20	2-Pentanone	
*21	Cyclohexanol	
*22	Ethylcyclopentane	
*23	2-Methyl-1-Pentanol	
*24	1,1-Dimethylcyclopentane	
*25	Cis-1,2-Dimethylcyclopentane	

* These hydrocarbons were only identified, not quantified

ml/min for 10 minutes. Trapped volatiles were then thermally desorbed at 250°C and backflushed to the GC column. Optimum results were achieved by temperature programming from 45°C to 200°C at 4°C/min with initial and final isothermal periods of 2 and 20 minutes, respectively. Carrier gas (nitrogen), hydrogen and air flow rates were 30, 30, 450 ml/min, respectively. Flow rates were checked by a bubble tube flow meter every day before analysis began. The injector port and detector temperatures were 250°C. Analysis time was approximately 60 minutes. Table 5.6 summarizes the GC conditions for the analysis of hydrocarbon components. At the end of each analysis, the column was cooled to 45°C for the next analysis.

A small amount of carry-over (less than five percent) of the heavier compounds was observed from the concentrator when a blank was run immediately after the concentrated sample. Thus, in order to have a clean trap for the next sampling, a blank was run on the same trap immediately after each analysis.

Sludge Volatility

A simple laboratory test was devised to measure the extent of hydrocarbon emissions to be expected from the land treatment of a given sludge. The basic idea of this test was to purge an inert gas (hydrocarbon-free air) through a small sludge sample and to sweep all volatile hydrocarbons out of the sample.

For the volatility test, a 25 ml impinger, compressed air and TLV Sniffer were used. Figure 5.6 depicts a diagram of volatility test set up.

The experimental procedure involved the following steps:

1. The empty impinger tube was first weighed.
2. The tube was filled with 15 ml of sludge sample

TABLE 5.6. PURGE & TRAP AND CHROMATOGRAPHIC CONDITIONS FOR THE ANALYSIS OF HYDROCARBON COMPONENTS

1.	Purge & Trap Conditions:	
	Prepurge Time	3 minutes
	Nitrogen Purge Flow	50 ml/min
	Purge Time	10 minutes
	Desorb Temperature	250°C
	Desorb Time	10 minutes
	Auxiliarly Temperature	200°C
	Vent Time	10 minutes
2.	GC Conditions:	
	Nitrogen Flow (carrier gas)	30 ml/min
	Air Flow	450 ml/min
	Hydrogen Flow	30 ml/min
	Detector Temperature	250°C
	Injector Port Temperature	250°C
	Oven Temperature	45°C Initial, to 200°C at 4°C/min
	Chart Speed	.5 in/min
	Attenuation	8

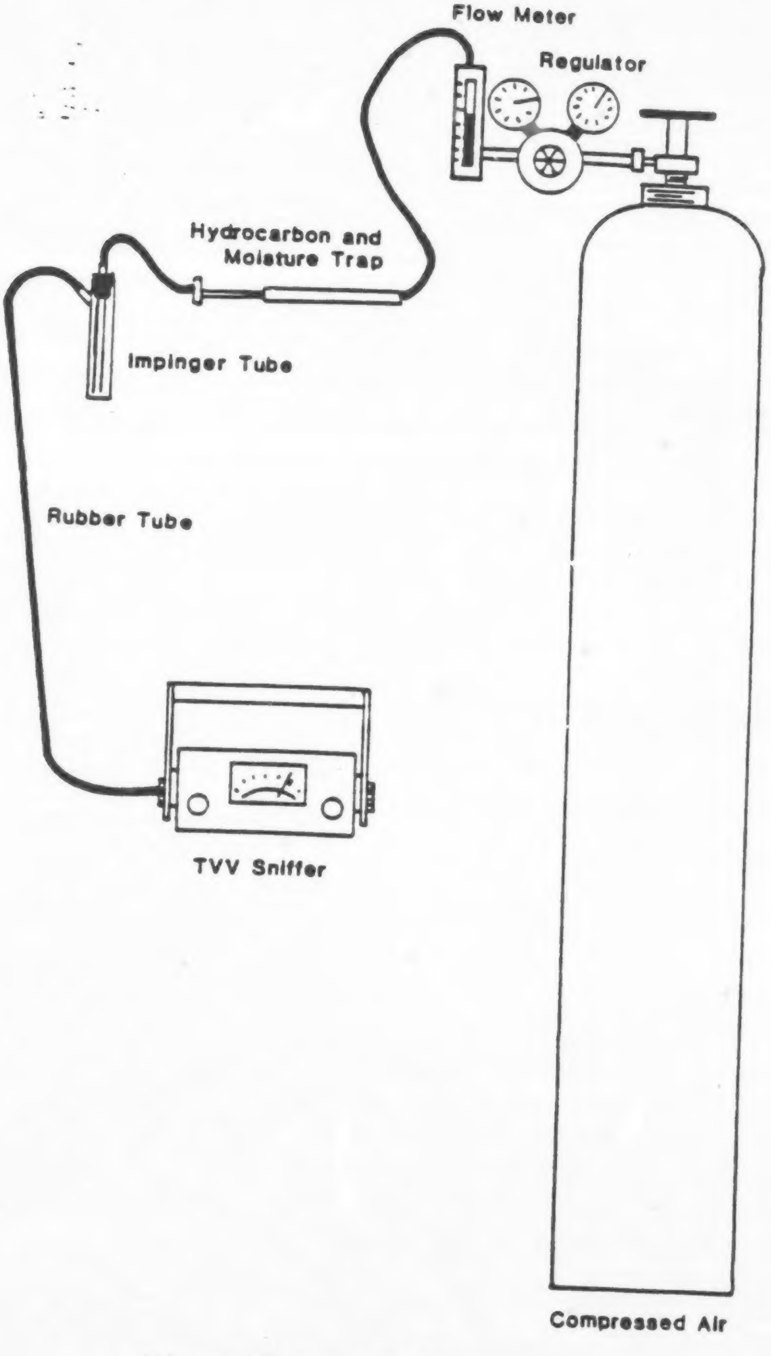

Flow Meter
Regulator
Hydrocarbon and Moisture Trap
Impinger Tube
Rubber Tube
TVV Sniffer
Compressed Air

Figure 5.6. Stripping test setup.

and weighed.

3. The stripping apparatus was set up.
4. The flow rate of air (purge gas) through the sludge sample was adjusted to 2 l/min in all stripping runs.
5. The hydrocarbon concentration in the stripping air was monitored with TLV Sniffer at 5 minute intervals for two hours, a constant time in all stripping tests.
6. The compressed air and TLV Sniffer were removed or disconnected from the impinger tube at 10-minute intervals and the impinger tube containing sludge was weighed.
7. The percentage volatile loss was calculated from the difference in sludge weight.
8. The data collected allowed for evaluation of the weight loss rate and a determination of the relationship between concentration (reading taken with TLV Sniffer) and weight volatilized.

Quality Assurance/Quality Control

A QA/QC program was implemented at the beginning of the project. This program had two main parts. Part 1 involved sample collection, transportation and storage, and Part 2 involved the determination of blanks, replicates and spikes.

Each sample collected was assigned an identifying code, which contained information on the plot no., date and type of sample collected. Samples were placed in a cooler immediately upon collection until they could be transported to the laboratory and refrigerated. The aqueous samples were stored in a refrigerator, at 4°C, until they were analyzed. Soil samples were collected in plastic bags and aqueous samples in borosilicate glass bottles with Teflon-faced screw caps. A log book of all site visits and samples collected was maintained. Aqueous samples to be analyzed for metals were adjusted to pH less than 2 with concentrated nitric acid as soon as they arrived at the laboratory. COD and pH analyses were performed on the samples within 24 hours of collection. All samples for priority pollutant analysis were extracted within one week of collection, and analyzed within one month of extraction.

Glassware used for priority pollutant analysis was solvent washed, detergent washed, rinsed with tap water, distilled water and oven-dried. The K-D (Kuderna-Danish apparatus) flasks and concentrators were also cleaned with chromic acid prior to each set of extractions. After each batch of samples from one site was run, the glassware was heated to 400°C in a furnace after the cleaning sequence described above.

Glassware for metal analyses was washed with detergent, and then acid-rinsed with nitric and hydrochloric acids. After a final rinse with distilled water, the glassware was oven-dried. Glassware used for other analyses were cleaned using standard laboratory cleaning procedures.

The quality control procedures used in the determination of priority pollutants centered mainly on the determination of blanks and the use of duplicate determinations. Pesticide grade solvents were used in all extractions. Spikes were also determined on the aqueous samples. No studies were done on recoveries from the different soil matrices, because of time and money restrictions.

The GC/MS system was tuned on a daily basis with perfluorotributylamine (PFTBA). Decafluorotriphenylphosphine (DFTPP) Standards were run to check the relative ion abundance. The mass spectrometer source was heated to a temperature of 274°C periodically to remove contaminants.

Duplicates, spikes and blanks were also run on the samples analyzed for metals.

Oil Content

Background soil samples were obtained from the field to represent the matrix of the soils to which the oily residues were applied. The background soil samples were spiked with a known amount of oily residue. The samples were extracted using the revised Soxhlet extraction procedure. The results are tabulated in Table 5.7. The mean recovery was found to be 96.2 percent.

TABLE 5.7. OIL RECOVERY FROM SPIKED SAMPLES

No.		% Oil Recovered	% Oil Applied
1		9.37	10.0
2		9.78	10.0
3		9.69	10.0
	Mean	9.62	10.0

Fractionation Analysis

Reference standards for quality control were obtained from EPA through their quality assurance program. The reference standard used was the Kuwait Crude Oil. Two analysts performed the extractions. The results of the recoveries by the two analyses are presented in Tables 5.8 and 5.9. The method of analysis was the ASTM - D2007.

TABLE 5.8. RESULTS OF ANALYSIS OF KUWAIT CRUDE OIL FOR QUALITY CONTROL - ANALYST 1

No.	Saturates	Aromatics	Polar Compounds	Asphaltenes
1	39.10	40.0	16.80	4.1
2	30.20	52.0	13.40	4.4
3	35.10	47.4	14.50	4.0
4	36.10	46.0	13.90	4.0
5	35.60	45.5	14.60	4.3
6	36.30	44.8	14.50	4.4
7	35.80	45.6	14.30	4.3
Mean	35.46	45.9	14.57	4.21
EPA Ref. Value	32.30	47.6	16.90	3.20

TABLE 5.9. RESULTS OF ANALYSIS OF KUWAIT CRUDE OIL FOR QUALITY CONTROL - ANALYST 2

No.	Saturates	Aromatics	Polar Compounds	Asphaltenes
1	33.00	48.4	14.30	4.3
2	32.80	47.7	15.30	4.2
3	36.00	44.9	14.90	4.2
4	35.60	44.8	15.20	4.4
5	32.30	47.7	15.70	4.3
6	33.60	47.0	15.20	4.2
7	34.20	46.4	15.20	4.2
8	33.80	47.0	14.90	4.3
9	33.50	46.7	15.70	4.1
10	32.00	48.4	15.10	4.5
Mean	33.68	46.9	15.15	4.27
EPA Ref. Value	32.20	47.6	16.90	3.2

pH - standardization of the meter before use and the determination of duplicates on soil samples. For aqueous samples only one determination per sample was possible.

Nitrate and phosphate - a standard was run with each set of samples to check the calibration curve, and one duplicate determination was carried out for each set of samples.

COD - quality control was by means of blanks and duplicates.

Volatile Organics

The quality assurance and quality control program for the volatile emission study was as follows:

1. The TLV Sniffer was calibrated every two months. The calibration was check with known concentrations of hexane prior to and after each sampling.
2. The sampling pump was calibrated before and after sampling, using a bubble flow meter.
3. Chain of custody forms were maintained for each sample.
4. Upon return from a sampling trip, each sample code and the results obtained from TLV Sniffer and other monitoring equipment were entered in a sample log book. This log was updated as samples proceeded through work up and analysis.
5. Vials for standards, glassware etc., were cleaned with soap and water, rinsed with demineralized water and methanol, and heated to 450-500°C to insure the removal of all traces of organic compounds.
6. After the preparation of a set of sampling cartridges, one cartridge was checked for background prior to the cartridge's commitment to field sampling.
7. All sampling cartridges were transferred to and from the field in an ice chest at a temperature of 4-10°C.
8. If two cartridges were used in series to check for breakthrough, they were separated and

sealed individually immediately after sampling to avoid errors arising from diffusion which might have occurred later.

9. The collected samples were analyzed within a week.

10. To insure the accuracy and precision of the data acquired, instrument and chromatographic performance were monitored as follows:

    (a) The linearity of the gas chromatograph was verified once a week. Three different concentrations of working calibration standards were used to obtain instrument response with thirteen compounds. When sample concentration versus instrument response was plotted, the result fell along a straight line.

    (b) A strict step-sequence of analysis was followed. At the start of each working day, the analysis cycle began with the blank (using organic-free water), the multi-component working standard and three samples. Each sample was followed by a blank. This way, the purge and trap and GC column performances were monitored every day. Running the blank also indicated that the syringe, needle and all lines from the purge and trap through the injection port and the FID were free of contaminants.

11. Each sample run by GC was logged into a notebook, detailing analysis conditions, compounds found and where the data were archived.

12. Periodically, duplicate samples were analyzed by GC-MS at the RSKERL EPA Laboratory in Ada, Oklahoma.

SECTION 6

RESULTS AND DISCUSSION

The primary emphasis of this project was to determine the rate of loss of oil from plots with a range of oil concentrations due to varying loading rates and frequencies. Secondary objectives were to determine losses due to migration and emissions to the atmosphere and to determine the presence and fate of certain priority pollutants. This section of the report presents the data collected during the study period and an interpretation of the data in terms of the stated research objectives. These objectives were discussed in Section 1. Reference should be made to Section 5 for a discussion of relevant analytical and experimental methods.

FATE OF OIL IN THE SOIL ENVIRONMENT

One of the stated research objectives was to establish loading rate and loading frequency guidelines. Thus, the objectives of this portion of the research were not only to establish the fate of oil in the soil environment, but to identify the optimum process conditions.

The mere disappearance of oil from the surface soil environment without regard to its ultimate fate is not the only criterion of optimization. It is important to identify those processes contributing to oil disappearance which are to be maximized and those which are to be minimized. Clearly, run-off, deep percolation and volatilization should be minimized, while biological degradation and photodegradation should be maximized. Run-on is controlled by placing an earthen berm around the active site. Deep percolation is minimized by selecting a site underlain with an impervious clay layer and by maintaining aerobic conditions in the zone of incorporation. Volatilization can be limited by subsurface injection if air pollution standards are violated by surface spreading, and by tilling under optimum environmental conditions.

Biodegradation of oil occurs principally in the zone of incorporation, with much less biological activity occurring at lower depths. Thus, the zone of incorporation may be considered a bioreactor in which conversion of substrate to various end-products occurs. This bioreactor operates in a quasi-completely mixed mode. Periodic measurements of substrate concentration within the bioreactor facilitate the evaluation of the rate of substrate disappearance from the zone of incorporation. Combined with information on other mechanisms of disappearance such as percolation, runoff, and volatilization, zone of incorporation oil content measurements allow evaluation of the biokinetic rates which are needed to optimize the process.

A fundamental measure of process kinetics is the kinetic order and rate with which reactions take place. If a reaction such as oil disappearance proceeds at a rate independent of the oil concentration or of any other reactant, then the reaction is said to be zero-order. Thus, if C, represents the concentration of oil at any time t; the disappearance of oil is described by the kinetic equation:

$$\frac{dC}{dt} = -K$$

where K is the zero-order reaction rate constant. A plot of oil content with time for a zero-order rate of disappearance is linear, with a slope equal to -K.

In contrast, first-order reactions proceed at a rate which is directly proportional to the concentration of the reactant. The following equation summarizes first-order reaction kinetics:

$$\frac{dC}{dt} = -KC$$

integration of this equation yields:

$$\ln \frac{C_o}{C_t} = Kt$$

thus, a plot of ln C versus time yields a linear plot for a first-order reaction.

Higher order reactions are possible and, in fact, highly likely considering the complex nature of the sludge and the variety of microorganisms which utilize the various fractions of organics. However, models based on higher order kinetics have not increased the precision in predicting rates of removal or removal efficiencies in other waste treatment studies. For the purposes of this study, pseudo first-order kinetics is sufficient to meet the objectives of the project.

Evaluation of Oil Content Data

Data from oil content analyses developed using methods previously described were recorded in laboratory notebooks and later entered into computer files for documentation and data manipulation. Information in each file consisted of sample date, plot sampled, values of oil content for each of the three composite samples from each plot, name of analyst, date of analysis, and reference to the laboratory notebook entry.

Raw oil content data from the zone of incorporation is sorted by plot number and ascending date and tabulated in Table A.2, Appendix A. In order to obtain a time series oil content 'history' for each plot, the analysis and loading data were merged to form the data sets presented in Table A.3, Appendix A.

These time series oil content histories include calculated values based on the amount of oil applied plus oil existing at a given time. Samples were generally collected immediately before application and the oil content determined. The oil content of this sample plus the oil applied equals the calculated after application oil content value. Similarly, if a plot was sampled following an oil application, the quantity of oil applied was subtracted to give a calculated before application value. In several cases a plot was sampled both before and after application to verify the amounts of oil applied.

Since the reliability of the analyses as estimates of the true mean oil content of a given plot is of primary importance, a screening methodology was used to identify any outlying values.

As discussed above in reference to the effect of sample preparation methodology on data variability, the coefficient of variation was computed for each set of analyses on a given plot and date. In the initial screening process, raw data for which the internal coefficient of variation was greater than 0.15 were flagged as possibly including an outlier. After loading data and analysis data were merged, the oil content data were graphed as a function of time for each test plot. These graphs may be found in Figures A.1 through A.32.

Several items are noteworthy with respect to Figures A.1 through A.32. Since oil content data prior to September 9, 1982 was taken before the oil analysis and sampling methods were finalized, the data was not reliable. Therefore, it was not possible to construct the portion of the load loss curves covering the first project year. Although data points are shown for all oil content data found in Table A.3, lines have only been drawn through those points which were used in data analyses as discussed below. Discontinuities are due to insufficient data. The dormancy period, period of low activity, which occurred during winter (elapsed days 486-598) was indicated with a solid line on those plots for which data adequate to describe this period. A dashed line was used on those plots which were only sampled at a time two or three months after the end of the dormancy period.

Based on a preliminary knowledge of the processes occurring, several criteria were developed with which anomalous values of oil content were identified. The criteria were based on apparent impossibilities such as the following:

1. Oil content should not increase without the addition of a sludge.
2. Though it was reasonable to assume that the samples taken after application could have a lower measured oil content than the calculated value (based on before application samples plus oil applied), the calculated oil content of value could not be lower than the measured value.
3. Degradation of the oil was assumed to follow zero or first-order kinetics, thus, if the form of the loss curve did not reflect this characteristic, the data was reviewed to determine why a difference existed.

If, when reviewing the data, such apparent impossibilities were found to exist, reference was made to the values of internal coefficient of the variation of the offending data. If a high Coefficient of Variation (C.V.) was found, reference was then made to the raw data to identify an outlier. If no outlier was present, then the anomaly was allowed to remain. If one of the raw data points was much different from the other values, a check was performed to see if any improvement in the C.V. could be made by dropping the outlier in the computation of the mean oil content. If dropping the outlier decreased the C.V., the outlier was dropped.

The time series oil content histories, corrected for outliers, is thus the basis for evaluation of the biodegradation process. The following discussion outlines the statistical techniques employed to describe the data and to compare different sludge loading treatments in terms of the objectives of process optimization.

Oil Content Data Evaluation

There were many field conditions encountered by the research team which adversely impacted the project. During much of the study period, wet weather limited the activities which could be performed at the research site. In particular, application and sampling frequencies were dictated by the weather. Differing antecedent soil conditions prevented full applications to several plots, including replicates of some plots which were fully loaded. Thus, there were many factors which precluded the use of the originally proposed factorial-type experimental design. Among these were: 1) the variation from nominal oil loadings received by the plots; 2) the irregular frequency with which the applications could be made; 3) the inability to apply the required amount of oily sludge to the plots receiving high rate - low frequency treatments; and 4) the inability to till some of the plots immediately following application of heavy oil loads, thus, introducing another process variable into the experimental design.

Only three sets of original plots received replicate treatment. The lack of replication had the combined effect of reducing the statistical significance of the experimental data, as well as vastly increasing the complexity of the data evaluation.

Despite the problems associated with a change in the statistical plan of analysis of the oil content data, several data analysis methods were identified which could be applied to the available data. These investigations were aimed at evaluation and comparison of loss rates based on loading rates and frequencies.

The following analyses were performed using the oil content data.

1. Total oil losses during the first year of the project were developed from the loading data and the oil content analysis performed in September 1982.
2. Total oil losses during the second year of the study were developed and compared with the first year's losses.
3. Total oil losses throughout the entire project until June 1983 were determined.
4. Loss rates and reaction order were investigated and rate coefficients were developed for several plots using oil content data collected in the Fall of 1982 and the following year.
5. Evaluation was made of the data comprising the cyclic loading/loss portions of the time series curves of several plots. This evaluation deals

primarily with the higher application frequency plots for which data covering more cycles exist. Though kinetic order cannot be determined from this data, both zero order and first-order rate coefficients were calculated.

6. Data on volatile emissions of certain plots was incorporated with the zone of incorporation loss data during the Fall of 1982, thus, separating this loss mechanism in the analysis. First order loss rates were recalculated based on this data.
7. The winter dormancy period was evaluated for several plots.

Based on availability of sufficient reliable data the plots were allocated for the particular investigation as shown in Table 6.1.

Total Oil Losses During First Study Year

The purpose of this analysis was to determine total oil losses and relate these losses to the factors which control them. Since the sludge loading data for each application is known, only one analysis at the end of the first year is required to compute the first year total losses for a particular plot.

For the purposes of discussion, the units of oil content and loading rate have been calculated on a percent oil based on the dry weight of the soil (% dwb), using constant plot dimensions of 2.75 m (9 ft) x 6.10 m (20 ft) x 0.30 m (1 ft) and a dry soil specific weight of 1282 kg/m^3 (80 lb/ft^3).

The total percent (dwb) of oil applied to each plot was calculated and the percent of oil remaining in the soil after 385 days subtracted to give the percent of oil lost. The gross loss was also computed in terms of per-

TABLE 6.1. PLOT ALLOCATION TO VARIOUS DATA EVALUATIONS

Total Losses	Loss Rates 1981-1982	Loss Rates 1982-1983	Cyclic Loading Period	Dormancy Period	Losses Other Than Emissions
	8	4	1	4	1
	10	5	2	5	4
	15	9	4	9	5
			5		
	16	10	6	10	6
	17	14	7	14	7
	21	15		15	
	22	20	9	20	
	23	24	11	24	
	24	25	13	25	
	28	29	14	29	
	29	30	18	30	
	30	34	20	34	
	31	35		35	
	35				
			25		
			26		
			32		

cent of the total first year loading. These values have been tabulated in Table 6.2. From this data it is evident that total losses increased with an increase in loading rates. Total loss (% dwb) as a function of total loading (% dwb) for the first study year indicated a good linear trend between these variables, correlation coefficient equal to 0.91. Regressing percent of total loading lost as a function of total loading resulted in a lower correlation coefficient.

Since the above analysis does not take into account the time the plots were loaded, a method was devised to relate total losses to a time-loading moment. Each individual loading was multiplied by the time interval from the loading date to the date of analysis (day 385) and the resulting products summed to yield a value which incorporates elapsed time until analysis with the antecedent loading. Total losses as a function of the total time-loading moment are shown in Figure 6.1. Total losses as a function of time-loading moments for all plots gave a correlation coefficient of 0.96 which indicates that the combined effect of total loading and elapsed time is greater than the effect of total loading alone. It is also evident that the total losses are greater for plots which received few heavy applications early in the first project year, than for plots which received more frequent low applications over the entire year.

Total Losses During Second Study Year

Total oil losses were computed for the second study year as presented in Table 6.3. A trend similar to that shown during the first study year is evident, with total losses roughly proportional to the sum of antecedent oil from the first year plus the applied oil during the sec-

TABLE 6.2. TOTAL LOSSES DURING FIRST STUDY YEAR

Plot	First Year Loading (% dwb)	Oil Content Analysis (% dwb)	Total Oil Loss (% dwb)	% of First Year Loading Lost (%)	Time-Loading Moment (%dwb*day)
1	9.61	7.79	1.82	19	1278
2	5.81	3.99	1.82	31	941
4	2.01	1.07	0.94	47	299
5	6.62	3.89	2.73	41	960
6	15.04	9.49	5.55	37	2014
7	5.08	3.08	2.00	39	691
8	19.03	8.18	10.85	57	5576
9	2.62	1.59	1.03	39	445
10	7.86	3.63	4.23	54	1352
11	3.93	2.59	1.34	34	538
13	5.36	3.58	1.78	33	822
14	2.01	1.61	0.40	20	231
15	7.86	4.04	3.82	49	1360
16	6.90	4.06	2.84	41	2201
17	6.90	2.75	4.15	60	2139
18	1.34	1.10	0.24	18	206
20	8.54	5.11	3.43	40	1196
21	14.90	6.34	8.56	57	4619
22	16.68	8.66	8.02	48	4687
23	17.44	9.72	7.72	44	3087
24	4.03	2.73	1.30	32	544
25	1.64	1.50	0.14	9	261
26	7.06	4.20	2.86	41	967
28	12.75	8.46	4.29	34	1733
29	11.00	5.79	5.21	47	1782
30	10.75	4.49	8.16	58	3069
31	6.90	2.00	4.90	71	2132
32	2.62	2.17	0.45	17	453
34	5.37	3.10	2.27	42	843
35	12.96	5.37	7.59	55	4070
36	12.62	8.42	4.20	33	2600
38	4.03	3.50	0.53	13	725

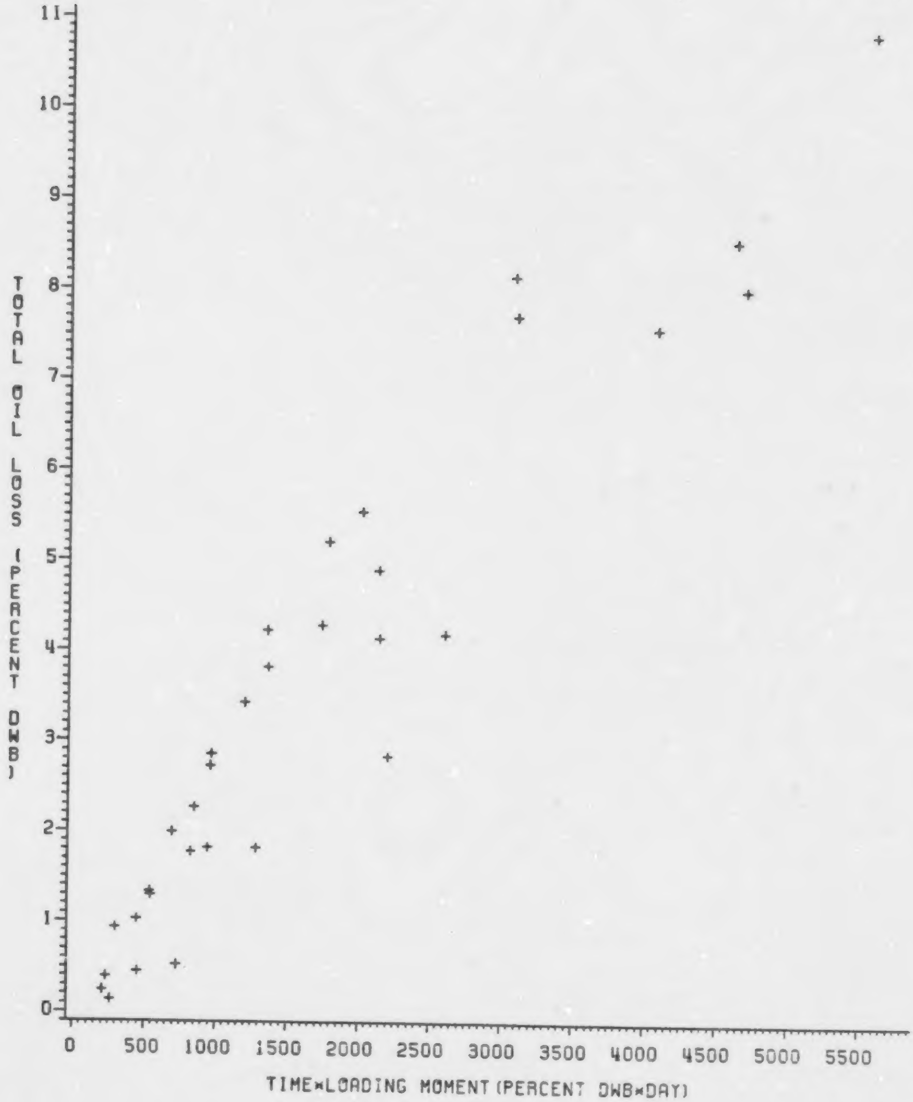


Figure 6.1. Total loss (% dwb) vs time loading moment, first year data.

TABLE 6.3. TOTAL LOSSES DURING SECOND STUDY YEAR

Plot	Initial Elapsed Time, (day)	Initial Oil Content (%dwb)	Total 2nd Year Loading (%dwb)	Day 657 Final Oil Content (%dwb)	Total Second Year Loss (%dwb)
1	384	7.79	10.43	10.82	7.4
2	384	3.99	4.97	6.76	2.2
4	384	1.08	2.12	1.62	1.58
5	384	3.89	8.26	7.00	5.15
6	409	9.49	5.00	8.16	6.33
7	384	3.08	3.45	4.94	1.59
8	385	8.18	7.74	9.68	6.24
9	397	1.59	2.28	3.05	0.82
10	385	3.64	6.90	6.85	3.69
11	384	2.59	4.60	4.57	2.62
13	384	3.58	3.84	4.51	2.91
14	384	1.61	2.28	2.12	1.77
15	385	4.04	6.90	7.88	3.06
16	385	4.07	3.45	5.43	2.09
17	385	2.75	1.72	7.84	1.63
18	397	1.10	1.45	1.39	1.16
20	384	5.11	5.76	5.46	5.41
21	385	6.34	7.47	7.12	6.69
22	385	8.66	5.75	8.57	5.84
23	385	9.72	4.23	6.40	7.55
24	385	2.73	3.45	4.13	2.05
25	385	1.50	0.58	1.33	0.75
26	384	4.21	5.00	5.06	4.15
28	385	8.46	11.50	11.32	8.64
29	385	5.79	11.50	9.98	7.31
30	385	4.50	3.45	2.51	5.44
31	385	2.00	1.72	1.87	1.85
32	384	2.17	2.18	2.27	2.18
34	384	3.10	2.88	4.19	1.79
35	385	5.37	5.75	5.24	5.88
36	385	8.42	3.97	7.32	5.07
38	385	3.50	3.45	4.11	2.84

ond year.

Second year total losses as a function of second year oil loadings yields a correlation coefficient of 0.81. Total losses as a function of the sum of the first year antecedent oil content plus second year oil loading yields a correlation coefficient of 0.94, indicating that total oil loss is a function of the total oil content not just that applied during the second year.

Total Losses Over Two Year Period

Total oil losses over the two year study period were evaluated in much the same way as the first year's data (Table 6.4). Oil content values determined for samples taken June 9, 1983 were subtracted from the total percent applied to each plot to give the percent lost over the approximate two year study period (657 days). Percent of the total oil loading lost was then computed. The average percent of oil lost per day was computed by dividing the percent lost by the number of days elapsed from the first application date until the June 9, 1983 analysis.

Analysis of this data revealed a strong linear relationship between average percent of oil lost per day and total percent applied over the study period. A plot of this data is presented in Figure 6.2. The correlation coefficient associated with a linear regression of percent dwb of oil lost per day on total oil loading was 0.95.

Time-loading moments, about the June 9, 1983, analysis date were computed for each plot as discussed for the first years loadings. Percent lost as a function of time-loading moment yielded an extremely high correlation coefficient of 0.99.

The total loss data for the first year, the second year, and for the entire study period indicates that oil

TABLE 6.4. TOTAL LOSSES DURING TWO YEAR STUDY PERIOD

Plot.	Time-Loading Moment (%dwb/day)	Percent dwb Lost (%dwb)	Percent of Total Lost (%)	Average Percent dwb Lost per Day (% dwb/day)
1	6358	9.22	46.0	0.014
2	3581	4.02	37.3	0.007
4	1326	2.52	60.8	0.004
5	4645	7.89	53.0	0.012
6	6858	11.88	59.3	0.018
7	2884	3.59	42.1	0.005
8	12306	6.15	63.5	0.026
9	1606	2.44	44.5	0.004
10	4954	7.91	53.6	0.012
11	2691	3.96	46.4	0.006
13	3127	4.68	50.9	0.007
14	1364	1.62	43.3	0.002
15	4978	6.88	46.6	0.011
16	4784	4.92	47.5	0.008
17	4363	5.79	67.1	0.010
18	905	1.39	49.9	0.002
20	4871	8.84	46.6	0.011
21	10186	15.69	68.8	0.024
22	10395	13.86	61.8	0.021
23	8552	14.24	65.7	0.023
24	2544	3.34	44.7	0.005
25	856	0.88	39.8	0.001
26	4139	6.98	58.0	0.011
28	8335	13.40	54.2	0.020
29	7209	12.51	55.6	0.019
30	5921	11.68	82.3	0.018
31	4363	6.75	78.3	0.010
32	1656	2.64	53.7	0.004
34	2951	4.05	49.2	0.006
35	7819	13.46	72.9	0.020
36	6709	5.23	41.7	0.008
38	2544	3.37	45.1	0.005

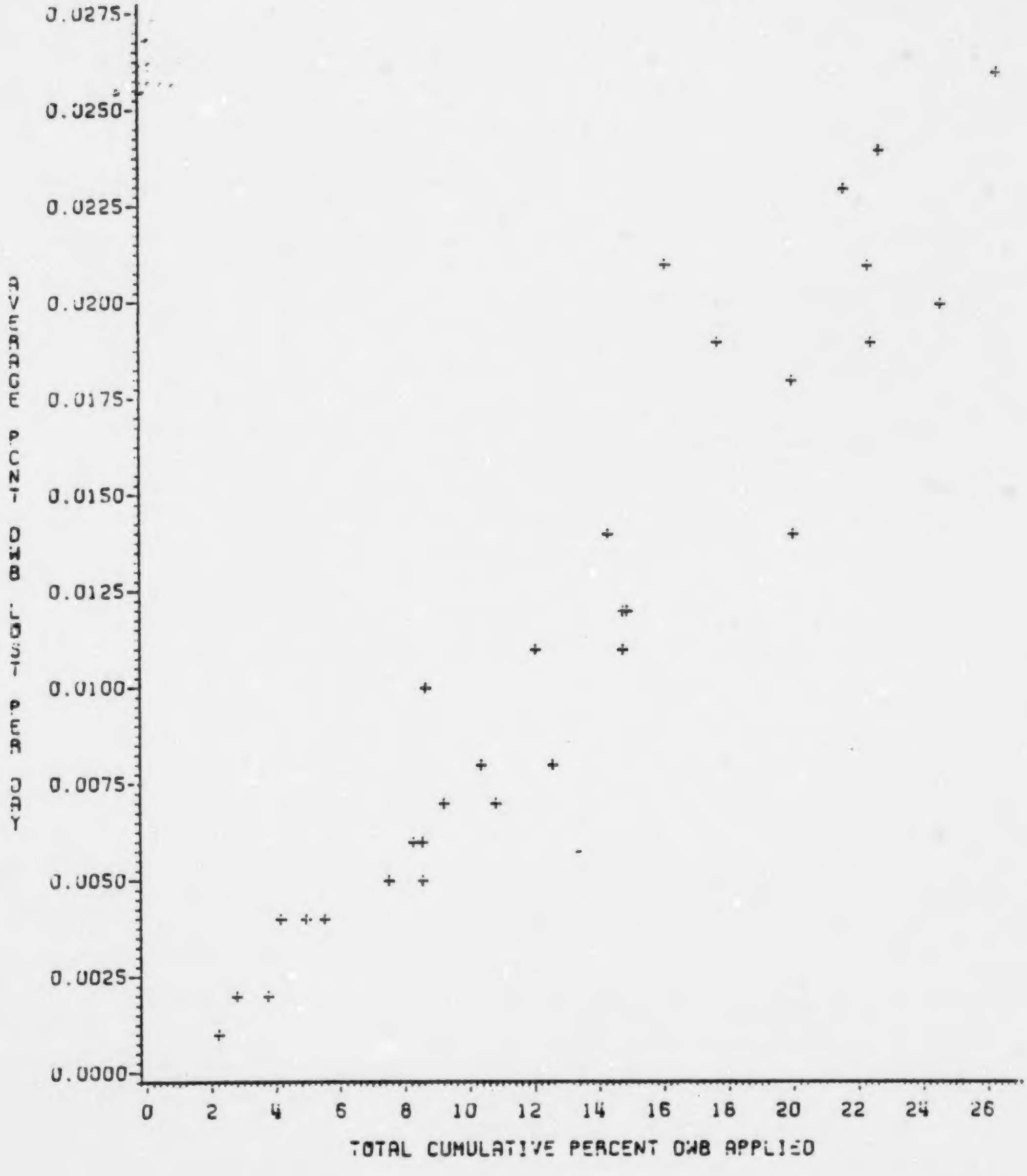


Figure 6.2. Percent (dwb) lost per day vs total percent (dwb) applied to date.

losses increase in proportion to the increase in total oil loadings. The time elapsed since application is also an important factor especially during the first few years until equilibrium is reached.

An average of 54 percent of the total oil applied disappeared during the overall study period of 657 days with a range from 37.3 to 82.3 percent. This contrasts the data presented in the first year for which the average percent of applied oil lost was equal to 39.6 percent with a range from 9 to 71 percent.

Kinetic Rate Evaluation for First Year

Several plots were selected for an investigation of kinetic order and loss rates at the end of the first study year. The criteria for selection was that there were at least three reliable oil content values available between the last application of the first year to the first oil application in the second year.

Data of the type required for this investigation was available for fourteen plots. For each of the plots, the mean oil content values as a function of elapsed time from the first application date yielded zero order slopes. Correlation coefficients were used to test goodness of fit. First order rates were obtained by evaluation of the natural logarithm of mean oil content as a function of elapsed time. The corresponding correlation coefficient obtained gives an indication of the goodness of fit.

The results of the regression analyses are given in Table 6.5. As can be seen from this data, plots 16, 17, 29, and 31 all showed fairly good linearity as both zero-order and first-order functions, with the first order kinetics appearing slightly more highly correlated. Though correlation coefficients are not as strong for the

TABLE 6.5. KINETIC ORDER AND LOSS RATES FOR FIRST STUDY YEAR

Plot	Elapsed Time (days)	Mean Oil Content (%dwb)	ln of Mean Oil Content	Zero Order		First Order	
				Rate	R^2	Rate	R^2
8	385	8.18	2.10	0.018	0.82	0.0025	0.86
	401	7.30	1.99				
	453	6.77	1.91				
10	385	3.64	1.29	0.0045	0.53	0.0013	0.53
	401	3.32	1.20				
	444	3.31	1.20				
15	385	4.04	1.40	0.0166	0.91	0.0046	0.91
	401	4.08	1.41				
	444	3.14	1.14				
16	385	4.07	1.40	0.011	0.98	0.0031	0.98
	401	4.00	1.39				
	453	3.33	1.20				
17	385	2.75	1.01	0.013	0.98	0.0058	0.99
	401	2.42	0.88				
	453	1.83	0.604				
21	385	6.34	1.85	0.021	0.78	0.0038	0.80
	401	5.13	1.64				
	445	4.80	1.57				
	453	4.62	1.63				

(continued)

TABLE 6.5. (continued)

Plot	Elapsed Time (days)	Mean Oil Content (%dwb)	ln of Mean Oil Content	Zero Order Rate	Zero Order R^2	First Order Rate	First Order R^2
31	385	2.00	0.693	0.0050	0.99	0.0027	0.99
	401	1.91	0.647				
	453	1.66	0.507				
35	385	5.37	1.68	0.025	0.88	0.0064	0.88
	401	4.44	1.49				
	444	3.87	1.35				
	453	3.66	1.30				
	486	2.48	0.91				

other plots investigated, the same trend favoring first order kinetics is suggested.

No clear relationship was established between first-order rate coefficients and mean initial oil content for the data in the first year. This was expected if the reaction kinetics were in fact first-order and thus independent of oil concentration.

The average first-order rate coefficients for the first year is equal to 0.0046 with a standard deviation of 0.0017. The highest first-order correlation coefficient correspond to the rate coefficients for plot 29 and 31 which both showed rate coefficients of approximately 0.003.

Kinetic Rate Evaluation for Second Year

Regression analysis was applied to data from several plots during the second year of the study, as was done for a portion of the first years data. In 1983, five plots were sampled 3-4 times throughout late spring and summer.

Table 6.6 presents the results of the determination of kinetic order and rate coefficients for the second study year. As with the first year data, there is somewhat greater correlation for first order kinetics than the corresponding zero order values.

An anomaly is present with respect to plot 30. An increase of 1.2 percent dwb occurred between day 657 and day 727. No outliers were found in raw oil content data from these two dates. The anomaly could not be explained and the correlation coefficient was very low, therefore, the data from plot 30 was neglected in the determination of the rate coefficients.

Neglecting the data for plot 30, the mean of the remaining four values is 0.0020 with a standard deviation

TABLE 6.6. KINETIC ORDER AND RATE COEFFICIENT FOR THE SECOND STUDY YEAR

Plot	Elapsed Time (days)	Mean Oil Content (%dwb)	ln of Mean Oil Content	Zero Order		First Order	
				Rate	R^2	Rate	R^2
4	627	2.25	0.811	0.007	0.74	0.0040	0.78
	657	1.62	0.482				
	727	1.44	0.365				
5	627	7.92	2.069	0.012	0.81	0.0017	0.83
	657	7.00	1.946				
	727	6.59	1.886				
29	627	9.81	2.283	0.022	0.87	0.0025	0.88
	657	9.98	2.301				
	727	7.84	2.059				
30	598	5.20	1.649	0.012	0.32	0.0029	0.24
	627	4.79	1.567				
	657	2.51	0.920				
	727	3.71	1.311				
35	598	7.82	2.056	0.021	0.77	0.0033	0.80
	627	6.40	1.856				
	657	5.24	1.656				
	727	4.97	1.604				

equal to 0.0010.

Assuming non-normal distributions for first-order for the first and second year's data, a non-parametric rank sum test (Mann-Whitney U-Test) was used to see if there was any significant difference between the means. At an $\alpha = 0.05$ there was found to be no statistical difference between the first year's mean first-order rate coefficient of 0.0046 and the second year's coefficient 0.0029.

Zero order and first order coefficients were computed for eight plots based on two values of the oil content data taken in 1983 (see Table 6.7). Determination of the correct kinetic order is not possible on these plots due to the fact that only two points are available with which to define the loss curve. The data were taken over a 30-day period and yielded an average first-order coefficient of 0.0058 with a standard deviation of 0.0039.

Evaluation of Cyclic Loading/Loss Data

An evaluation of the cyclic loading/loss portion of the 1982 oil content data was made for plots identified in Table 6.1. In general, the two values of oil content used to describe each loss cycle were the calculated value after application and the final oil content analysis taken prior to the next oil loading.

The data were clustered into four groups according to time of the year in which the cycle occurred. This was done to minimize the effects of differing climatic and environmental conditions. A summary of the rate coefficients for the cyclic loading/loss data is given in Table 6.8.

A comparison of coefficients was made between groups to assess the possible effect of differing environmental conditions. No clear relationships were established

TABLE 6.7. RATE COEFFICIENTS FOR 1983 (BASED ON 30 DAY INTERVAL IMMEDIATELY AFTER APPLICATION)

Plot	Elapsed Time (days)	Oil Content (%dwb)	Zero Order Loss Rate (%/day)	First Order Loss Rate (ln %/day)
9	627	3.62	0.019	0.0057
	657	3.05		
10	627	8.29	0.048	0.0064
	657	6.85		
14	627	2.70	0.019	0.0081
	657	2.12		
15	627	8.47	0.020	0.0024
	657	7.88		
20	627	7.01	0.052	0.0083
	657	5.46		
24	627	4.55	0.014	0.0032
	657	4.13		
25	627	1.86	0.018	0.0118
	657	1.33		
34	627	4.22	0.001	0.0002
	657	4.19		

TABLE 6.8. LOSS RATE COEFFICIENTS FOR CYCLIC OIL LOSS DATA (1982)

Plot	Interval	Initial Oil Content	Final Oil Content	Number of Days	Zero Order (%dwb/day)	First Order (ln %dwb/day)
1	1	10.72	9.61	25	0.044	0.0044
11	1	3.74	3.23	24	0.021	0.0061
26*	1	5.45	4.44	24	0.042	0.0085
2	2	4.12	3.57	14	0.039	0.0102
4	2	1.55	1.31	14	0.017	0.0120
5*	2	5.37	4.90	14	0.034	0.0065
7	2	3.95	3.69	14	0.019	0.0049
9*	2	2.16	1.99	14	0.012	0.0059
13	2	4.01	3.97	14	0.003	0.0007
14	2	1.58	1.36	14	0.016	0.0107
18	2	1.39	1.04	14	0.025	0.0207
20*	2	6.42	5.47	14	0.068	0.0114
25	2	1.49	1.41	14	0.006	0.0039
32	2	2.58	2.18	14	0.029	0.0080
2**	3	5.77	5.10	34	0.020	0.0036
6	3	11.65	10.07	34	0.046	0.0043
7	3	4.84	4.54	36	0.008	0.0018
13	3	4.92	4.78	36	0.004	0.0008
20	3	7.39	6.56	36	0.023	0.0033
25**	3	1.69	1.55	34	0.004	0.0025
32	3	2.84	2.43	34	0.012	0.0046
2	4	6.34	5.08	33	0.038	0.0067
9	4	3.10	2.98	33	0.004	0.0012

(continued)

TABLE 6.8. (Continued)

Plot	Interval	Initial Oil Content	Final Oil Content	Number of Days	Zero Order (%dwb/day)	First Order (ln %dwb/day)
13	4	5.74	4.73	33	0.031	0.0059
18	4	1.79	1.45	33	0.010	0.0064
26	4	6.42	2.77	33	[0.111]	[0.0255]
32	4	3.01	1.84	33	0.035	0.0149

*
** Determined from hypothetical 'after' value
Determined from measured 'after' value
[ ] Indicates suspect data

based on this data.

Average first-order rate coefficients for the cyclic loading-loss data was found to be 0.0065 with a standard deviation of 0.0046. The rate coefficients are higher than those for the first-year as submitted in Table 6.5 or the second year as given in Table 6.6. That the coefficients are higher in the period immediately following application than during later periods suggests that either some oil fractions are preferentially degraded, or that loss of oil by some mechanism other than biological degradation, possibly volatilization, occurs simultaneously with biodegradation.

Incorporation of Volatile Emissions in Oil Loss Data Evaluation

Oil losses due to volatilization represent a significant fraction of the total losses. To determine the magnitude of oil losses via volatilization a study was performed which is discussed later in this section. The results are merged with total losses as discussed below to assess the impact on rate coefficients. Volatile emissions from five plots were measured as hexane and computed in terms of oil lost over various time periods following application. Table 6.9 presents this data.

As a percent of oil applied, the highest losses of oil due to volatilization occurred following the application to plot 4 on September 23, 1982. Total oil lost due to volatile emissions in 20 days following this application was 8.34 kg or approximately 23 percent of the total oil applied. The greatest net loss of oil between applications occurred for plot 5 between September 23 and October 12, 1982. Thirteen kg were lost which represents a volatile loss of 0.20 percent dwb, approximately half of the net loss determined by the oil content analysis. Similarly, for other plots volatile emissions for other plots during a short period of time immediately following application, accounted for up to 65 percent of the total losses of oil from a plot. Table 6.10 gives a breakdown of total and volatile oil losses for several plots.

Rate coefficients were calculated based on total losses and on total losses minus volatilization which is considered to be predominately of biological origin. These results are given in Table 6.11. The removal of volatile losses from the total losses in the computation of the rate coefficients had the effect of decreasing the variance as well as lowering the mean coefficient from 0.0057 to 0.0033. Also, comparing these two values with those recorded in Tables 6.5 to 6.7, it is interesting to note that the 0.0033 value closely approximates the mean value of 0.0046 for the first year and 0.0029 for the second year taken over a long period after application and the 0.0057 value corresponds to data taken over a short period of time immediately after application. Therefore, the differences in the coefficients determined from data taken over the cyclic portion of the curves immediately after application and those determined from a longer period several weeks after application can be attributed to the loss of volatile organics.

Dormancy Period

As can be seen from several of the figures in Appendix A, a period of low oil loss occurred between day 486 and day 627, as compared to the loss rates following this period.

The reduction in oil loss rates during the dormancy period may be due to several factors. This period corresponds to the winter and early spring months between December and May, and thus low temperature may be partly responsible for a decrease in biological activity in the

TABLE 6.9. TOTAL VOLATILE LOSS FROM FIELD PLOTS

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/19/82	1	13	1	230.3	195.755	-	.220	.923	3.073	8.173	29
08/17/82	1	13	2	230.3	195.755	8.0	.070	.320	2.090	6.990	24
09/10/82	1	13	3	230.3	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	1	13	4	262.2	157.320	13.6	.530	2.550	6.050	9.790	18
11/02/82	1	13	5	262.2	157.320	12.5	.903	3.990	8.700	11.700	15
11/17/82	1	13	6	206.53	163.158	9.1	.130	.630	2.130	4.530	33**
Subtotal				1421.83	1065.063		1.906	9.033	24.843	52.433	153
07/13/82	4	3	1	45.31	38.513	-	.070	.390	1.910	5.849	31
08/13/82	4	3	2	45.31	38.513	8.4	.063	.386	1.452	4.992	41
09/23/82	4	3	3	60.49	36.294	14.0	.340	2.020	6.280	8.340	19
10/12/82	4	3	4	45.31	27.186	13.8	.100	.860	3.230	4.010	20
11/02/82	4	3	5	60.49	36.294	12.5	.260	1.610	3.910	5.220	15
11/17/82	4	3	6	47.67	37.659	9.1	.056	.400	1.400	3.800	33**
Subtotal				304.58	214.459		.889	5.666	18.182	32.211	159
07/13/82	5	10	1	150.58	127.993	-	.150	.720	2.660	7.240	30
08/12/82	5	10	2	150.58	127.993	8.5	.090	.600	2.200	8.390	42
09/23/82	5	10	3	201.67	121.002	14.0	.810	3.100	8.150	13.123	19
10/12/82	5	10	4	201.67	121.002	13.8	.320	1.360	5.260	11.260	20
11/02/82	5	10	5	262.67	157.320	12.5	.330	1.820	5.370	8.290	15
11/17/82	5	10	6	158.86	125.499	9.1	.130	.650	1.850	4.250	33**
Subtotal				1125.56	780.809		1.830	8.250	25.490	52.553	159

(continued)

TABLE 6.9. (continued)

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.*	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/20/82	6	13	1	230.30	195.755	-	.203	1.013	3.163	8.263	28
08/17/82	6	13	2	230.30	195.755	8.0	.070	.310	2.100	6.950	24
09/10/82	6	13	3	230.30	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	6	13	4	262.20	157.320	13.6	.500	2.510	6.040	9.780	18
11/02/82	6	13	5	262.20	157.320	12.5	.903	3.990	8.700	11.600	15
11/17/82	6	13	6	206.53	163.158	9.1	.130	.630	2.130	4.520	33**
Subtotal				1421.83	1065.063		1.859	9.073	24.933	52.343	152
07/20/82	7	6	1	90.62	77.027	-	.110	.680	2.490	6.800	28
08/17/82	7	6	2	90.62	77.027	8.0	.045	.280	1.700	5.530	37
09/23/82	7	6	3	121.01	72.606	14.0	.560	3.310	6.930	11.110	19
10/12/82	7	6	4	121.01	72.606	13.8	.130	1.000	3.550	10.210	35
11/17/82	7	6	5	95.33	75.310	9.1	.093	.510	1.610	4.010	33**
Subtotal				518.59	374.576		.938	5.780	16.280	37.660	152
TOTAL				4792.39	3499.97		7.422	37.802	109.728	227.200	775
% Total sludge volatilized:							.154	.788	2.289	4.740	
% Total oil volatilized:							.212	1.080	3.135	6.491	

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* Application number

** No. of days from 11/17/82 to 12/20/82

d = days.

TABLE 6.10. PORTION OF TOTAL LOSS AS VOLATILE EMISSIONS

Plot	Application Date	Number of Days from Application to Soil Sample	Total % dwb Lost	Number of Days for Volatilization	% dwb Volatilized	% of Total Loss Volatilized
1	9/10/82	25	1.11	34	0.172	.15
4	9/23/82	14	0.74	19	0.127	.17
5	9/23/82	14	0.47	19	0.20	.42
6	10/14/82	34	1.58	18	0.149	.9
7	9/23/82	14	0.26	19	0.170	.65
7	10/12/82	34	0.30	35	0.156	.52

TABLE 6.11. FIRST ORDER LOSS RATES CORRECTED FOR VOLATILE LOSSES

Plot	(1) Initial Oil Content (% dwb)	(2) Oil Volatilized (% dwb)	(1)-(2) Oil Content After Volatilization (% dwb)	Final Oil Content (% dwb)	No. Days	Total *Biological (day^{-1})	1st Order Rate Co-efficient
1	10.72	0.17	10.55	9.61	25	.0044	.0037
4	1.55	0.13	1.42	1.31	14	.0120	.0059
5	5.37	0.20	5.17	4.90	14	.0065	.0038
6	11.65	0.19	11.50	10.07	34	.0043	.0039
7	3.95	0.17	3.78	3.69	14	.0049	.0017
7	4.84	0.16	4.68	4.54	34	.0019	.0009
Mean						.0033	

* Biological - Total minus volatilization

zone of incorporation. In addition to the temperature effects, saturated conditions existed in most of the test plots during this time. This high moisture content resulted in anaerobic conditions as evidenced by noxious odors which were produced when the soil was disturbed. It was observed that earthworms which had been prolific in the zone of incorporation prior to the wet weather were found in large numbers coming to the surface or floating dead in water on the surface of the plots. Under these conditions biological oxidation of the oil is extremely limited. A secondary effect of the saturated conditions was the inability to till the plots which only compounded the problem.

FRACTIONATION STUDIES

An investigation into the fate of four oil fractions was performed for plots 30 and 35 which had received moderate sludge loadings. Samples were fractionated into asphaltenes, saturates, aromatics, and polar compounds. The methodology used for fractionating the sludges and recovered oils was discussed in Section 5.

Since the oil was fractionated prior to application, the relative amounts of each fraction applied was known. Amounts of the total oil and the individual fractions applied to each study plot are given in Table 6.12. As can be seen from this table, the first two applications to each plot were made with the same batch of sludge (Batch I) and the third application was made using a different sludge (Batch IV).

Oil recovered from soil samples taken from the zone of incorporation was fractionated and calculated as a weight percent of the recovered oil. The raw fractionation data is presented in Table A.4, Appendix A. There were three samples for fractionation for each sample

TABLE 6.12. AMOUNTS OF OIL AND OIL FRACTIONS APPLIED TO PLOTS 30 and 35

Plot No.	Elapsed Day	Applied Oil (% dwb)	% Asph. In Oil (%)	% Asph. In Soil (% dwb)	% Sat. In Oil (%)	% Sat. In Soil (% dwb)	% Arom. In Oil (%)	% Arom. In Soil (% dwb)	% Pol. In Oil (%)	% Pol. In Soil (% dwb)
30	0	3.85	1.50	0.06	60.50	2.32	27.90	1.07	10.10	0.39
30	151	6.90	1.50	0.10	60.50	4.17	27.90	1.93	10.10	0.70
30	486	3.45	4.43	0.15	30.15	1.04	37.15	1.28	28.26	0.98
35	0	6.15	1.50	0.09	60.50	3.72	27.90	1.72	10.10	0.62
35	151	6.81	1.50	0.10	60.50	4.12	27.90	1.90	10.10	0.69
35	486	5.75	4.43	0.25	30.15	1.73	37.15	2.14	28.26	1.62

date. Mean values were computed for each sample after deleting any outliers. Mean values are given in Table 6.13.

Sludge loadings to plots 30 and 35 were made on elapsed day 0, 151, and 486. Soil analyses were performed on days listed in Table 6.13. Based on the available data, total losses for each fraction were computed for two periods. The first period was from the first day through day 486 (prior to the third sludge application). The second period was from day 486 to day 657. Losses for the first period were computed based on the sum of the first two loadings and the analysis of day 486. The total losses for the second period were computed as the sum of the residual concentration of each fraction based on the analysis for day 486 plus the loading of that day minus residual for day 657. Total loss data are summarized in Table 6.14.

As can be seen from Table 6.14, the highest total loss during the first period for both plots occurred for the saturates fraction, followed by aromatics, polar compounds and asphaltenes. First period losses as a percentage of the total applied and calculated as shown in Table 6.14 were highest for saturates followed by aromatics, asphaltenes, and polar compounds. It should be noted that the first period losses for most fractions were fairly high due to the fact that the sludge applications were made in the first five months of the sixteen month period.

Second period losses were found to differ substantially from those of the first period. The most surprising difference was the decrease in the losses of the saturates fraction. All fractions with the exception of polar compounds showed lower losses during the second period than the first. The relative magnitude of the

TABLE 6.13. MEAN CONCENTRATIONS OF OIL FRACTIONS - PLOTS 30, 35.

Elapsed Day	Oil In Soil (%dwb)	Asph. In Soil (%dwb)	Sat. In Soil (%dwb)	Arom. In Soil (%dwb)	Pol. In Soil (%dwb)
385	4.50	0.21	2.10	1.38	0.81
401	3.15	0.19	1.28	0.89	0.79
444	2.85	0.25	0.86	0.77	0.96
486	1.94	0.07	0.34	0.68	0.74
598	5.20	0.28	1.65	1.37	1.90
627	5.10	0.30	-	-	-
657	2.51	0.11	0.84	0.74	0.87
385	5.38	0.34	2.25	1.36	2.29
401	4.37	-	1.90	-	1.62
444	3.87	0.34	1.09	0.98	1.45
486	2.48	0.11	0.92	0.88	0.95
598	8.70	0.54	3.23	1.76	3.01
627	6.52	0.45	-	-	-
697	5.24	0.28	2.17	1.12	1.67

TABLE 6.14. TOTAL LOSSES* OF OIL FRACTIONS

	Plot 30		Plot 35	
	Period 1	Period 2	Period 1	Period 2
Oil Applied	10.75	3.45	12.96	5.75
Sample Oil	1.94	2.51	2.48	5.24
Oil Loss	8.81	2.88	10.48	2.99
% Loss	82	53	81	36
Asphalt Applied	0.16	0.15	0.19	0.25
Sample Asphalt	0.07	0.11	0.11	0.28
Asphalt Loss	0.09	0.11	0.08	0.08
% Loss	56	50	42	24
Sat. Applied	6.49	1.04	7.84	1.73
Sample Sat.	0.34	0.84	0.52	2.17
Sat. Loss	6.15	0.54	7.32	0.08
% Loss	95	39	94	4
Arom. Applied	3.00	1.28	3.62	2.14
Sample Arom.	0.68	0.74	0.88	1.12
Arom. Loss	2.32	1.22	2.74	1.90
% Loss	77	62	76	63

(continued)

TABLE 6.14 (continued)

	Plot 30		Plot 35	
	Period 1	Period 2	Period 1	Period 2
Pol. Applied	1.09	0.98	1.31	1.62
Sample Pol.	0.74	0.87	0.95	1.67
Pol. Loss	0.35	0.85	0.36	0.90
% Loss	32	49	27	35

* All values % dwb in soil unless specified.

individual fraction losses were highest for aromatics followed by polar compounds, asphaltenes and saturates. Losses of polar compounds increased for both plots during the second period. The second period was only approximately 170 days consisting of approximately four months of relative dormancy during which time the cold weather and saturated conditions were responsible for low overall oil losses.

The composition of the sludge applied just prior to the second period was also different than that applied during the first period. The saturates content of Batch IV was less than half that of Batch I, and as compared to Batch I, all of the other fractions were from 33 to 295 percent higher.

Anomalous increases in concentration of asphaltenes (pentane insoluble compounds), saturates, and polar compounds were found following the third application of sludge. Although these increases were not expected they can be explained and have been noted by other researchers (Meyers and Huddleston, 1979). The time period during which the increases occurred, coincided with cold weather and saturated soil conditions. Therefore, anoxic conditions existed with a possibility of anaerobic decomposition.

Walker et al., (1976) characterized the pentane insoluble fraction using computerized mass spectrometry as carboxylic acids, ketones, esters and porphyrins. Waksman (1927) has shown that anaerobic decomposition produces various acids, such as acetic, butyric and lactic, and alcohols, such as ethyl and butyl and in some cases acetone. Ojinsky and Umbreit (1959) showed that the anaerobic decomposition of aromatic ring compounds produces acids, saturated hydrocarbons, alcohols and ketones. Evans (1977) delineated the anaerobic decomposition of the benzene nucleus under three different sets of biological conditions. The three conditions are: anaerobic photometabolism of benzoate by Athiohodaceae, anaerobic metabolism of dichlorophenol, giving rise to quinolines; and quinolines observed in the presence of fungal phenoloxidase in soil (Liu et al., 1981, Rosazza 1982).

During the time period when an increase in polar compounds was seen, phenol, 2 nitrophenol and pentachlorophenol, as well as benzene, nitrobenzene, and isophorone, were detected in the soil matrix.

Nonenzymatic transformation of aromatic and phenolic compounds into other polar compounds, such as xenobiotic compounds, is also possible, due to the alteration of the physico-chemical environment by variations of pH, temperature, redox potentials and other factors (Rosazza). Enzymatic conversion of organic sulfur compounds to sulfoxides in sterile soils were observed (Chin et al., 1970, Rosazza 1982). Sulfoxidation of carboxin by the fungus Utilago mayolis was observed in the soil by Lyr et al., (Rosazza 1982).

Thus, the relatively low apparent losses of polar compounds may be due to the production of these compounds as by-products of the degradation of saturates and other compounds as has been suggested by several researchers. The complex and dynamic nature of the microorganism population, and the complex nature of the organic substrates contained in the sludges makes evaluation of the actual degradation rates very difficult. Thus, the losses reported in Table 6.15 and loss rates as discussed below and recorded in Table 6.16 only reflect the apparent net losses.

First-order rate coefficients were computed for both periods. First period coefficients were based on data

TABLE 6.15. TOTAL OIL AND OIL FRACTION LOSSES

	Plot 30	Plot 35
Oil Applied	14.2	18.71
Sample	2.51	5.24
Loss	11.69	13.47
% Loss	82	72
Asph. Applied	0.31	0.44
Sample	0.11	0.28
Loss	0.20	0.16
% Loss	65	36
Sat. Applied	7.53	9.57
Sample	0.84	2.17
Loss	6.69	7.40
% Loss	89	77
Arom. Applied	4.28	5.76
Sample	0.74	1.12
Loss	3.54	4.64
% Loss	83	81
Pol. Applied	2.07	2.93
Sample	0.87	1.67
Loss	1.20	1.26
% Loss	58	43

TABLE 6.16. FIRST-ORDER RATE COEFFICIENTS FOR OIL FRACTIONS

		Rate Coefficient (K) (day^{-1})			
Plot	Period	Asph.	Sat.	Arom.	Pol.
30	1	0.0310	0.0170	0.0059	-
30	2	0.0160	0.0114	0.0097	0.0130
35	1	0.0260	0.0140	0.0040	0.0055
35	2	0.0110	0.0104	0.0086	0.0104

taken during the last one-hundred days of the 486 day period. Coefficients for the second period were developed from data taken after the winter dormancy period. The first-order coefficients for each fraction by plot and study period are given in Table 6.16. As can be seen from this table, the coefficients for the first period were higher for the saturates and asphaltenes fractions than the corresponding second period values, with aromatics and polar compounds having higher coefficients in the second period. Comparing plots 30 and 35 it is interesting to note that as the total oil applied increases the net loss also increases which is consistent with data from all other plots. However, the efficiency and the rate coefficients decrease with increasing oil concentrations. The decrease in efficiencies is explainable in that efficiencies for all waste treatment systems is a function of loading rates i.e., efficiency decreases with a increase in loading rate. The coefficients for plot 30 were 10-45 percent higher than the corresponding values for plot 35. This trend is not supported by data from the other plots. As stated previously there was no relation between rate coefficients and oil concentrations. It was noted that rate coefficients were highest for asphaltenes, followed by saturates, polar compounds and aromatics.

Asphaltenes show greater rate coefficients than other fractions because as the asphaltenes degrade other fractions were formed. Whereas, the other fractions, even though they degrade, were being produced as degradation products of asphaltenes, thereby showing a lower coefficient. The asphaltenes (measured as pentane insoluble compounds) produced during anoxic conditions were probably carboxylic acids, ketones, esters, aldehydes and alcohols (Walker et al., 1976). Therefore, as soon as the plots were tilled after the anoxic period, there was an immediate and rapid depletion of all compounds, which were readily amenable to degradation under aerobic conditions.

The above results of oil content and fractionation show that oil and the associated fractions degraded with time. The degradation of oil and fractions occurred predominantly in the summer and fall months. An inhibition period was observed during winter months, when there was no appreciable degradation for total oil content - even though the individual fractions showed increases and decreases. During the winter months saturates, asphaltenes and polar compounds showed increases. The increases were due to the anaerobic decomposition of oil. However, aromatics were found to degrade into other fractions even during winter months. Asphaltenes and polar compounds were found to degrade with time; which is contrary to the studies reported in the literature.

The oil losses for this study was found to be in agreement with that reported in the literature (Table 6.17). The loss of fractions presented in Table 6.18 ranged from 36 to 39 percent for the two year period.

UNSATURATED ZONE MONITORING

The results of the oil content analysis in the unsaturated zone are presented in Table 6.19. The results show that there was no significant migration below the zone of incorporation. The results of the oil content on elapsed day 231 (4/7/82), show that at a depth of from 30-40 cm (12-16 in) the oil concentration was in the range of 0.13 to 0.63 percent dwb. Inclement weather conditions did not permit the tilling of the plots and may have led to some vertical oil migration. However, analysis of the unsaturated zone at the end of 406 days

TABLE 6.17. OIL LOSSES - COMPARISON WITH REPORTED VALUES

Reference	% Oil Losses/Year
Huddleston and Myers	72
Raymond et al.	485-90
Present study	45-81

TABLE 6.18. OVERALL LOSSES OF OIL FRACTIONS

	Plot 30	Plot 35
Oil Applied	14.2	18.71
Sample	2.51	5.24
Loss	11.69	13.47
% Loss	82	72
Asph. Applied	0.31	0.44
Sample	0.11	0.28
Loss	0.20	0.16
% Loss	65	36
Sat. Applied	7.53	9.57
Sample	0.84	2.17
Loss	6.69	7.40
% Loss	89	77
Arom. Applied	4.28	5.76
Sample	0.84	2.17
Loss	6.69	7.40
% Loss	83	81
Pol. Applied	2.07	2.93
Sample	0.87	1.67
Loss	1.20	1.26
% Loss	58	43

TABLE 6.19. OIL CONTENT ANALYSIS OF THE UNSATURATED ZONE

Plot No.*	Depth of Sampling	Date	Oil Content Wt. % on Dry Wt. Basis
30-1	30-40 cm	4/7/82	0.13
30-2	30-40 cm	4/7/82	0.29
35-1	30-40 cm	4/7/82	0.33
35-2	30-40 cm	4/7/82	0.63
30-1	91-107 cm	9/30/82	0.04
30-2	152-163 cm	9/30/82	0.03
35-1	61-71 cm	9/30/82	0.05
35-2	86-102 cm	9/30/82	0.02
35-3	117-132 cm	9/30/82	0.09
35-4	152-163 cm	9/30/82	0.03
30-1	61-76 cm	7/15/83	0.20
30-2	97-107 cm	7/15/83	0.15
35-1	61-76 cm	7/15/83	0.15
35-2	107-122 cm	7/15/83	0.05

* The 1 and 2 after the plot no. represent duplicate samples.

shows that the oil content values below 40 cm were similar to the background oil levels.

VOLATILE EMISSIONS FROM LAND TREATMENT OF PETROLEUM RESIDUES

The atmospheric emissions from land treatment of petroleum sludge were assessed in this study. This section presents analyses and results. The first part is a summary of the sniffer data for laboratory and field experiments. The second part presents the results of statistical analyses. The third part shows the significance of results from the standpoint of air pollution. The fourth part presents the results and interpretation of the gas chromatography data.

LABORATORY AND FIELD STUDIES

Stripping Tests

Stripping tests were carried out to measure volatility of the sludge and to estimate weight loss of individual sludge components due to volatilization from land treatment operations. The procedures have been described in Section 5.

Hydrocarbon concentrations in the stripping gas were monitored every five minutes and weight loss of sludge was measured every ten minutes during at least a two-hour test run. Because of differences in volatility of the different batches of sludge, a stripping test was conducted each time the application was made. The volatility of these sludges was calculated and is presented in Table B.1, Appendix B. Table 6.20 presents the stripping test results for the last batch of sludge. This sludge was also used for laboratory experiments. In this test air was purged into the sludge sample at 2.02 l/min. These data were used to construct curves of cumulative calculated TLV Sniffer responses as a function of time

TABLE 6.20. STRIPPING TEST RESULTS

Stripping Time (min.)	Reading from sniffer		Area Count	Mass of Volatiles (mg)	Cummulative Mass (mg)	Wt** Loss (mg)	Cummulative Wt. Loss (mg)
	Direct (ppm)	Calculated (mg/min.)					
<1	3200	22.76					
5	2000	14.23					
10	1500	10.67	37	148	148	278.4	278.4
15	1200	8.54					
20	1000	7.11	20.5	82	230	169.3	447.7
25	900	6.40					
30	600	4.27	14.5	58	288	154.8	602.5
40	380	2.40	9.0	36	324	87.3	689.8
45	310	2.21					
50	300	2.13	5.5	22	346	85.3	775.1
55	230	1.63					
60	190	1.35	4.0	16	362	65.0	840.1
65	140	.99					
70	110	.78	3.0	12	374	61.7	901.8
80	80	.57	1.9	7.6	381.6	36.7	938.5
90	30	.21	1.0	4.0	385.6	8.3	946.8
100	20	.14	.7	2.5	388.1	4.5	951.3
110			.2	.1	388.1	3.9	955.2

* Air flow through the sludge = 2.02 l/min.

** Initial wt. of sludge = 11045.3 g

% wt. loss of sludge = 8.5

and sludge weight loss (Figures 6.3 and 6.4). These curves can be used to relate the emission rate to the weight loss for other experimental tests using the same sludge.

As might be expected, the rates of emission and weight loss were time-dependent. For example, the initial weight loss rate was 278.4 mg/10 min. and declined to about 3.9 mg/10 min. within 110 minutes. During the same period the volatile losses measured by the Sniffer was 22.76 mg/min. initially and dropped to 0.14 mg/min. after 100 minutes. The percentage of weight lost during a 110 minute test period for the last batch of sludge, was calculated to be 8.65 percent.

In view of the results obtained, it was decided to conduct an experiment with water under the same conditions as the sludge sample to estimate water loss. During the test period, the water loss was insignificant (approximately 0.12 percent) compared to the volatile loss.

Total Volatile Emission

Throughout the sampling and testing period, the laboratory and field analytical results were transferred to a master log. The data was then stored on a tape in an IBM computer system. Preparation of the raw data into usable form involved converting ppm reading from sniffer to g/hr of total volatiles. Tables B.1 and B.2 in Appendix B present calculated concentrations of total volatile hydrocarbons for field and laboratory experiments. From these data, calculated concentration-time plots, such as those shown in Figures 6.5 and 6.6, were generated. The patterns observed in these graphs are typical of all loading rates and all temperature ranges, although the emission rates at any time vary with loading rates and environmental conditions.

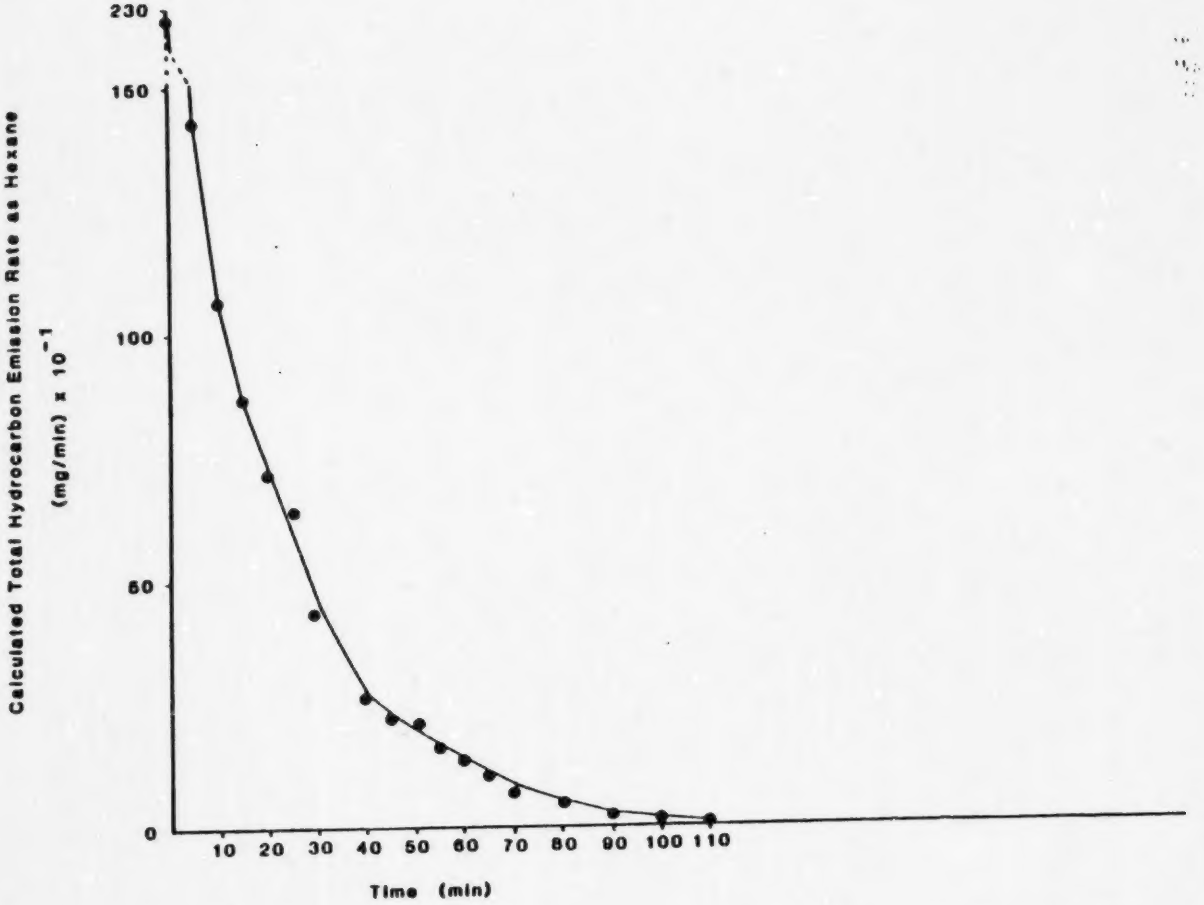

Figure 6.3. Calculated total volatile emission of sludge sample vs time.

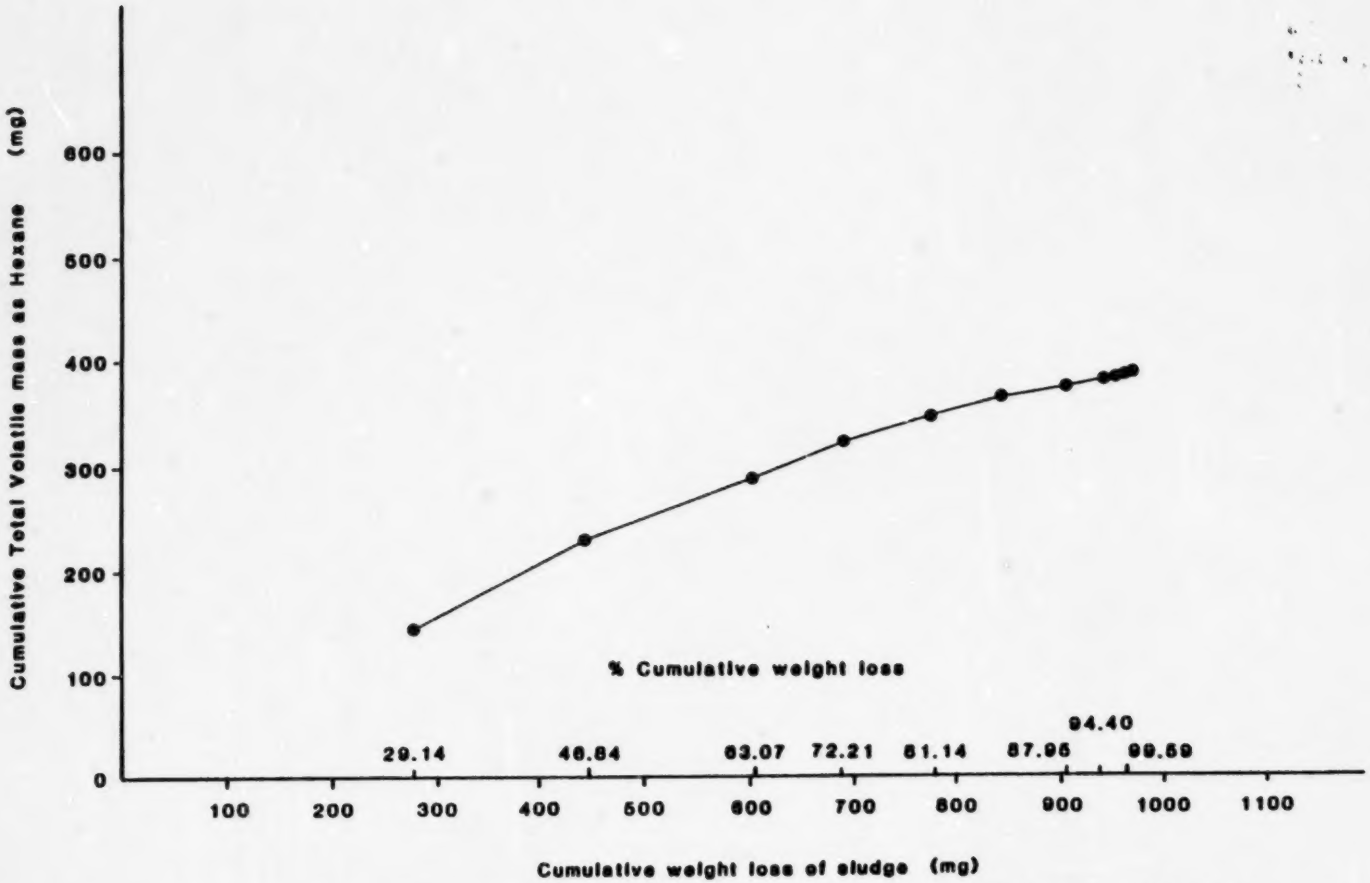

Figure 6.4. Relationship between cumulative total volatile mass and sludge weight loss.

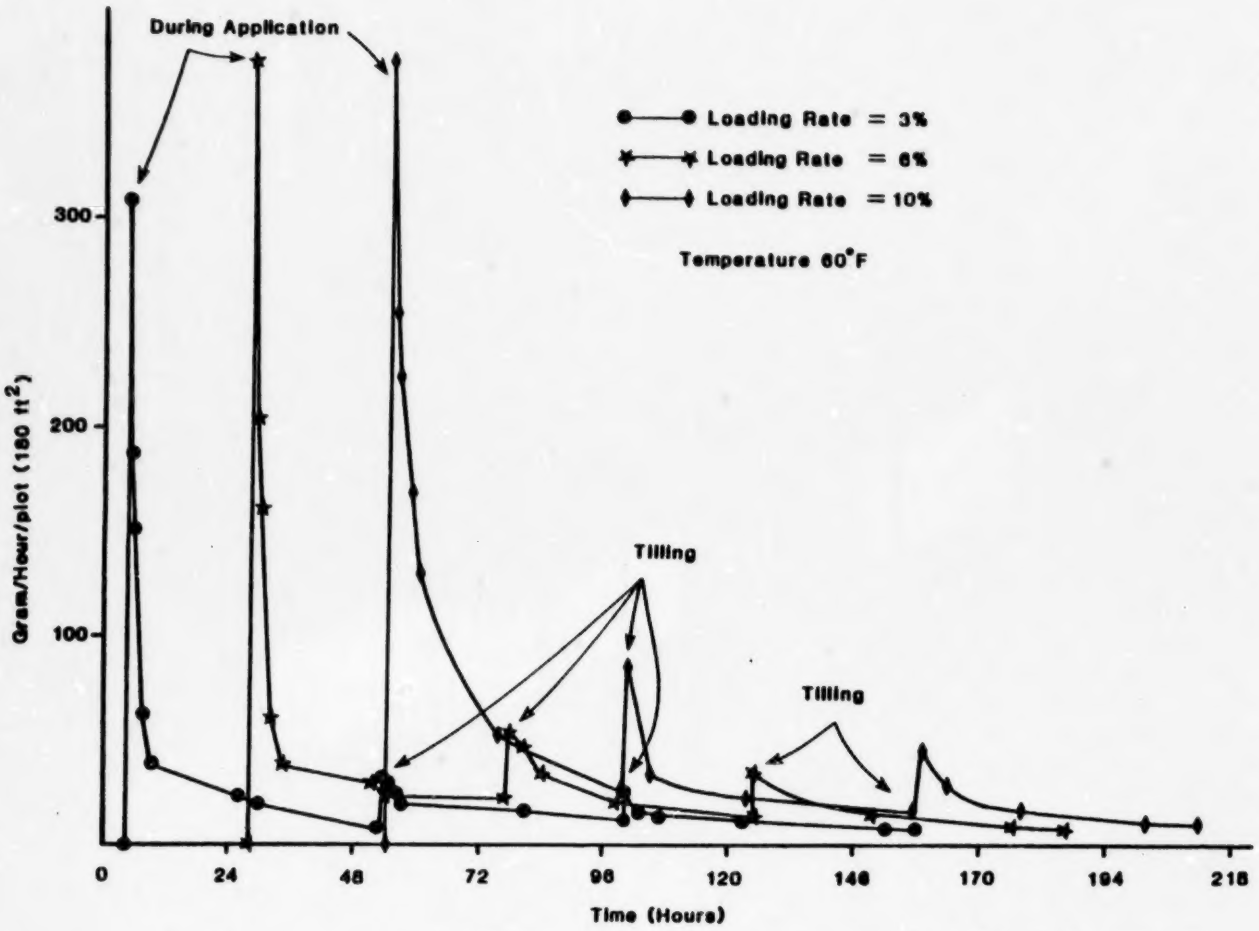

Figure 6.5. The effect of loading rate and tilling frequency on emission in laboratory experiments at 60°F.

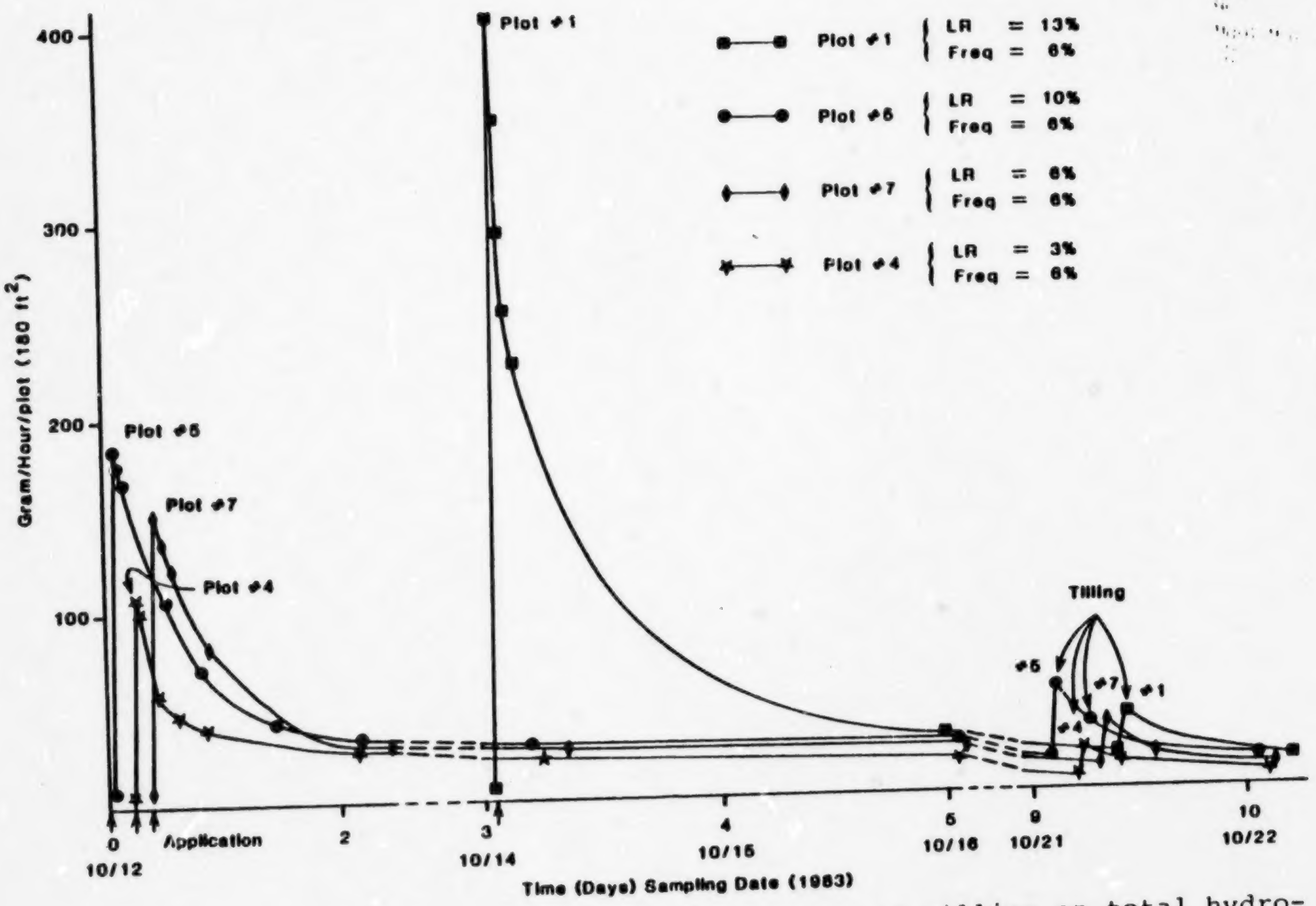

Figure 6.6. The effect of loading rate and tilling on total hydrocarbon loss in field studies.

These figures show that in the laboratory a very sharp rise in the hydrocarbon concentration in the air appeared immediately after sludge application began. The maximum hydrocarbon concentration was reached during the application or very shortly thereafter. However, an abrupt decline from the maximum concentration and a gradual approach to a lower concentration followed. These results are similar to the results achieved by Minear et al. (1981).

In the field, because of losses which occurred during sludge application, and the time which elapsed before the chamber could be placed over the soil after application, a more gradual rise in hydrocarbon concentration was noted in the sampling chamber.

The hydrocarbon concentration in most tests dropped to less than 50 percent of its maximum value within two hours after application. Therefore, it was evident that comparisons of the concentrations for the first two hours and for the first day would give a quick estimation of the relative hydrocarbon emission losses. Figures 6.7 and 6.8 show the maximum concentration and rate of decrease in emission in the first two hours from application at three different temperatures and loading rates.

The areas under the time-concentration curves were determined at two hours, one day and seven day intervals from application for field and laboratory data, and from application to application for field data only. From these areas the losses were calculated for each loading rate. Table 6.21 gives the summarized data by plot number and loading rate for all the samples collected from the field plots. This table can be used to obtain an estimate of volatile losses at various time intervals and sludge loading rates. Included in the table are the date of application of sludge, percent volatility of

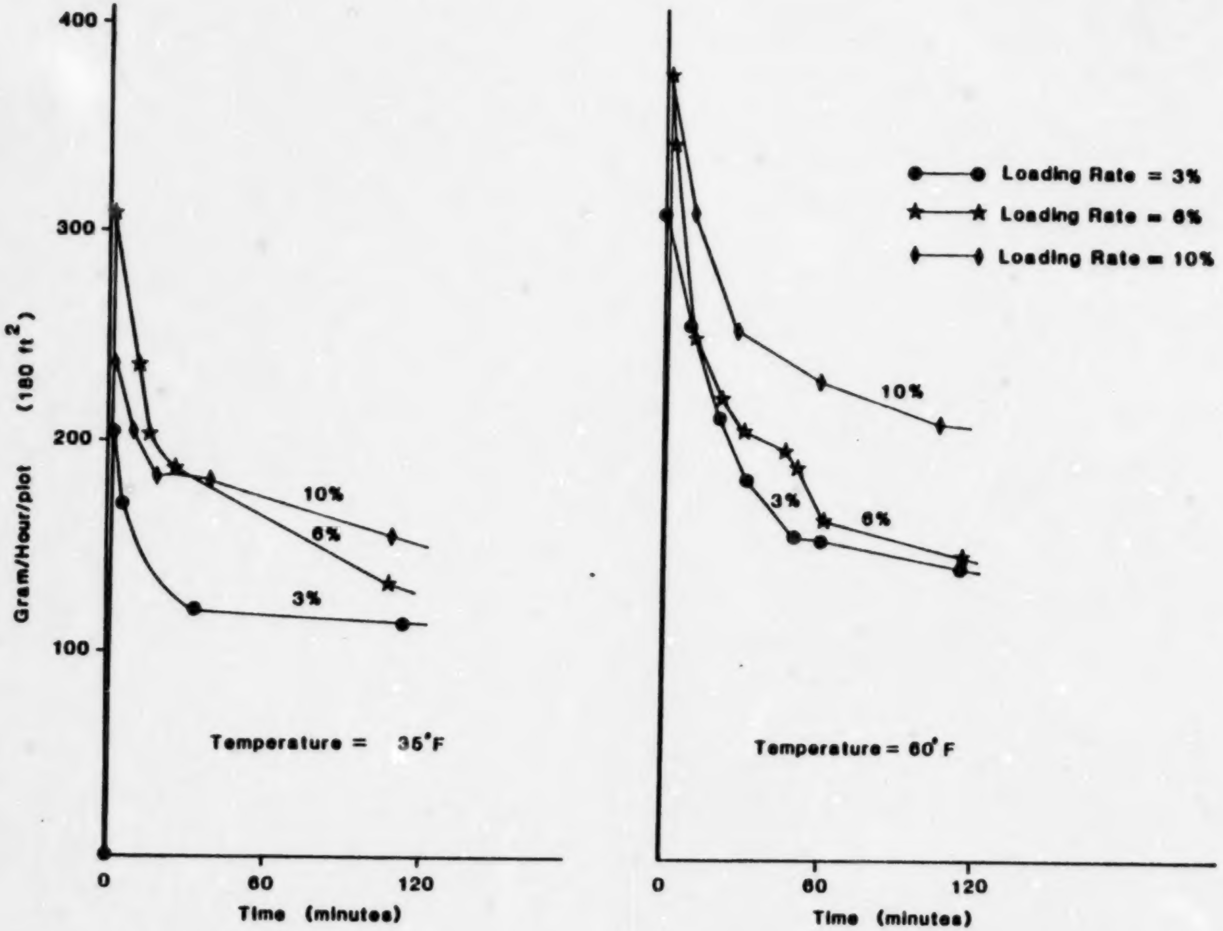

Figure 6.7. Rate of emission of volatiles in first two hours after application at temperature 35^{O}F and 60^{O}F.

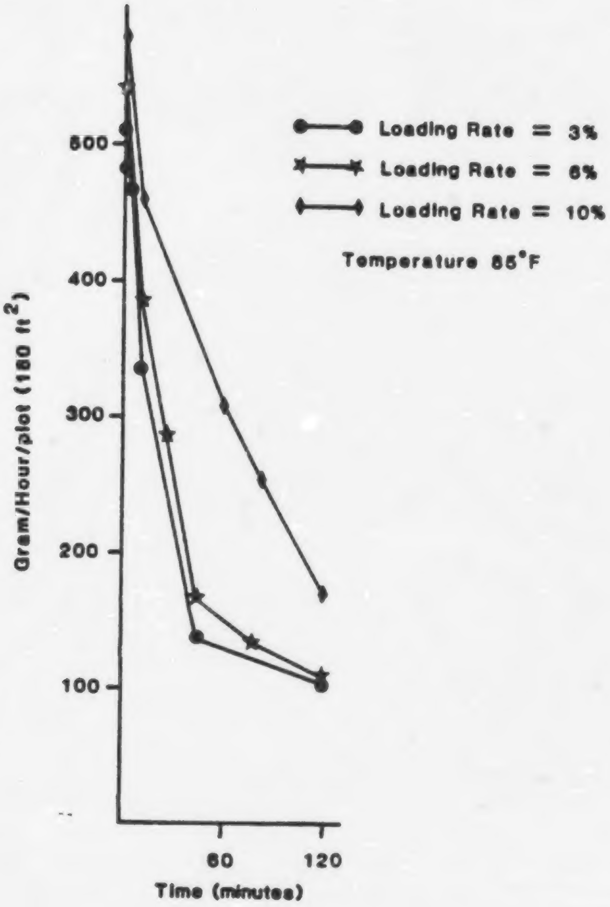

Figure 6.8. Rate of emission of volatiles in first two hours after application at temperature 85°F.

TABLE 6.21. TOTAL VOLATILE LOSS FROM FIELD PLOTS

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/19/82	1	13	1	230.3	195.755	-	.220	.923	3.073	8.173	29
08/17/82	1	13	2	230.3	195.755	8.0	.070	.320	2.090	6.990	24
09/10/82	1	13	3	230.3	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	1	13	4	262.2	157.320	13.6	.530	2.550	6.050	9.790	18
11/02/82	1	13	5	262.2	157.320	12.5	.903	3.990	8.700	11.700	15
11/17/82	1	13	6	206.53	163.158	9.1	.130	.630	2.130	4.530	33**
Subtotal				1421.83	1065.063		1.906	9.033	24.843	52.433	153
07/13/82	4	3	1	45.31	38.513	-	.070	.390	1.910	5.849	31
08/13/82	4	3	2	45.31	38.513	8.4	.063	.386	1.452	4.992	41
09/23/82	4	3	3	60.49	36.294	14.0	.340	2.020	6.280	8.340	19
10/12/82	4	3	4	45.31	27.186	13.8	.100	.860	3.230	4.010	20
11/02/82	4	3	5	60.49	36.294	12.5	.260	1.610	3.910	5.220	15
11/17/82	4	3	6	47.67	37.659	9.1	.056	.400	1.400	3.800	33**
Subtotal				304.58	214.459		.889	5.666	18.182	32.211	159
07/13/82	5	10	1	150.58	127.993	-	.150	.720	2.660	7.240	30
08/12/82	5	10	2	150.58	127.993	8.5	.090	.600	2.200	8.390	42
09/23/82	5	10	3	201.67	121.002	14.0	.810	3.100	8.150	13.123	19
10/12/82	5	10	4	201.67	121.002	13.8	.320	1.360	5.260	11.260	20
11/02/82	5	10	5	262.67	157.320	12.5	.310	1.820	5.370	8.290	15
11/17/82	5	10	6	158.86	125.499	9.1	.130	.650	1.850	4.250	33**
Subtotal				1125.56	780.809		1.830	8.250	25.490	52.553	159

(continued)

TABLE 6.21. (continued)

Date of Appl.	Plot No.	Nominal Loading Rate	Appl. No.	Sludge Applied (kg)	Oil Applied (kg)	Volatility of Sludge (%)	Total Loss in-2 hr. (kg)	Total Loss in-1 d (kg)	Total Loss in 7 d (kg)	Total Loss Since Appl. (kg)	Total No. of Days Since Appl.
07/20/82	6	13	1	230.30	195.755	-	.203	1.013	3.163	8.263	28
08/17/82	6	13	2	230.30	195.755	8.0	.070	.310	2.100	6.950	24
09/10/82	6	13	3	230.30	195.755	7.8	.053	.620	2.800	11.250	34
10/14/82	6	13	4	262.20	157.320	11.6	.500	2.510	6.040	9.780	18
11/02/82	6	13	5	262.20	157.320	12.5	.903	3.990	8.700	11.600	15
11/17/82	6	13	6	206.53	163.158	9.1	.130	.630	2.130	4.520	33**
Subtotal				1421.83	1065.063		1.859	9.073	24.933	52.343	152
07/20/82	7	6	1	90.62	77.027	-	.110	.680	2.490	6.800	28
08/17/82	7	6	2	90.62	77.027	8.0	.045	.280	1.700	5.530	37
09/23/82	7	6	3	121.01	72.606	14.0	.560	3.310	6.930	11.110	19
10/12/82	7	6	4	121.01	72.606	13.8	.130	1.000	3.550	10.210	35
11/17/82	7	6	5	95.33	75.310	9.1	.093	.510	1.610	4.010	33**
Subtotal				518.59	374.576		.938	5.780	16.280	37.660	152
TOTAL				4792.39	3499.97		7.422	37.802	109.728	227.200	775
% Total sludge volatilized:							.154	.788	2.289	4.740	
% Total oil volatilized:							.212	1.080	3.135	6.491	

* Application number

** No. of days from 11/17/82 to 12/20/82

d = days

sludge, the amount of sludge and equivalent oil applied each application, the calculated losses at different times, and the total number of days between applications.

During a six-month test period in the field (July 13 - December 20, 1983) total volatile losses for each plot individually, and for all five plots combined, were also calculated. The volatile loss is given in kg/16.7 m^2 (180 ft^2) of plot area.

The results indicate that of the 4792 kg (10560 lb) of sludge applied to plots 1,4,5,6 and 7, 3500 kg was oil. During the six months following the first application, 4.7 percent was lost through volatilization to the atmosphere which is equivalent to 6.5 percent of the total oil applied. The percentage of loss, estimated on the basis of total sludge and total oil applied, is given in Table 6.21. The total percentages of losses in two hours, one day and seven days from application were estimated at .15, .79 and 2.29, respectively. Since the loss rate decreases with time, the percentage of loss in about six months was found to be approximately twice the percentage of loss in seven days from application.

The percentages of total loss in two hours, one day and seven days from application were also calculated on the basis of total loss over the 152 to 159 day period. The results are presented in Table 6.22. Figure 6.9, generated from Table 6.22 also shows the percentage of total loss as a function of time for different loading rates. Approximately 50 percent of total volatiles was lost in seven days after application from each plot. Therefore, the seven-day period chosen for laboratory experiments was an adequate time period to use in comparing the effects of variables on emission.

From Table 6.21 it is evident that the higher loading rates resulted in higher volatile losses, assuming

TABLE 6.22. PERCENT OF TOTAL LOSS FROM DIFFERENT LOADING RATES AT DIFFERENT TIMES FROM APPLICATION

Plot #	% Loading Rate	Total # * of days	Total Loss kg	% of Total Loss in two hours	one day	seven days
4	3	159	32.211	2.75	17.59	56.44
7	6	152	37.660	2.49	15.34	43.22
5	10	159	52.553	3.48	15.69	48.50
1	13	153	52.433	3.63	17.22	47.38
6	13	152	52.343	3.55	17.33	47.63

* Total # of days that total losses were calculated for each plot starting from first application (7/13/1982-7/20/82) to the last sampling date (12/20/82).

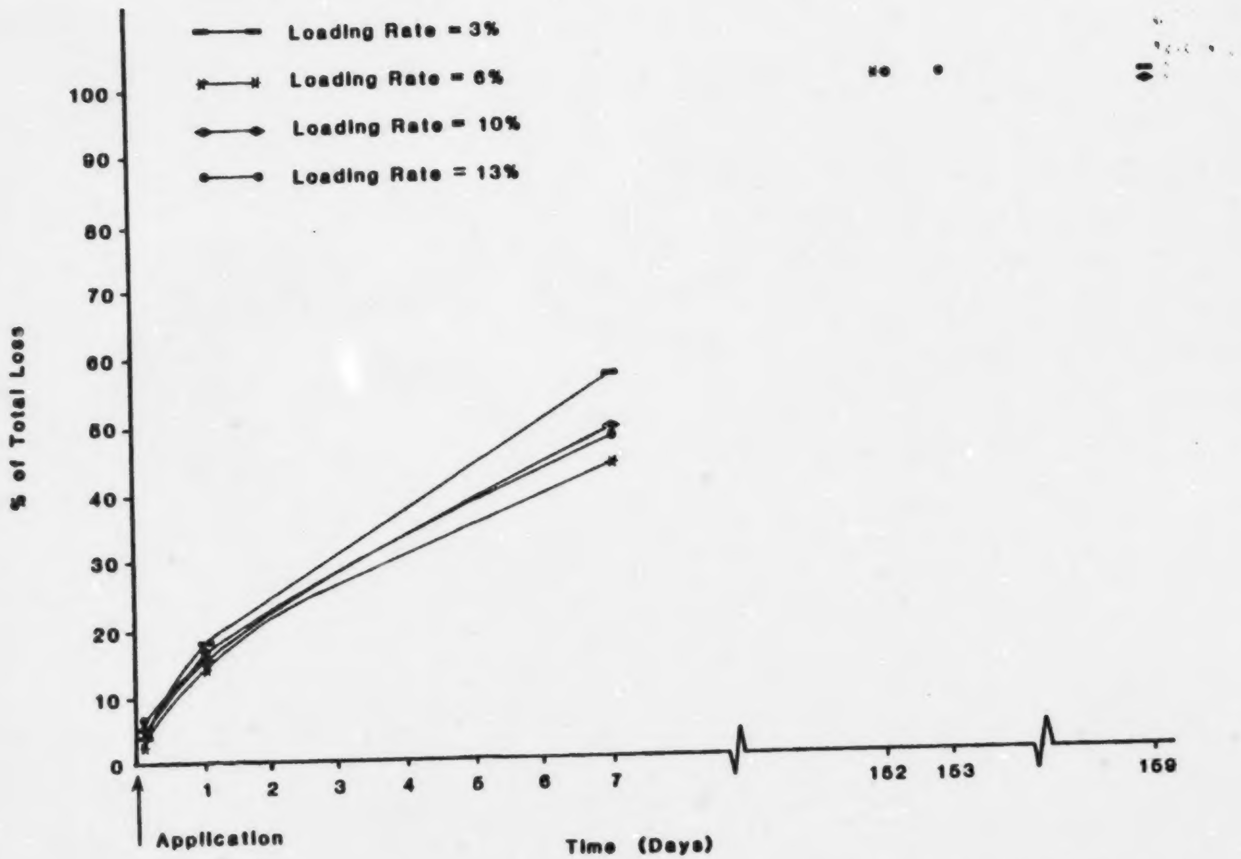

Figure 6.9. Percent volatile loss at different loading rates vs time.

all other conditions were constant. However, losses from plot 5 were higher than expected for two reasons. First, there was a misapplication on 11/2/82 of 262 kg (13 percent loading rate) instead of 206 kg (10 percent loading rate). The second reason was that on 9/23/82 application to plot 5 was made from a new batch of sludge with high volatility (14 percent), while on 9/10/82 old sludge with low volatility (7.8 percent) was applied to plots 1 and 6. These facts have resulted in about 4-5 kg more volatile loss from plot 5 than expected. Occurrences of this kind compound the problems of predicting volatile losses. The range of total volatile loss was from a low of 3.80 to a high of 13.12 kg. The arithmetic means and standard deviation of total loss for each plot separately and all five plots together are presented in Table 6.23.

Another important discovery (Table 6.21) was the variation of volatile losses within each loading rate from one application to another. This variation could be explained primarily on the basis of volatility of different batches of sludges. It was found that volatility of the sludge is a very important factor in determining emission rates. For this reason a stripping test was developed in an attempt to provide a quantitative measure of relative volatility which could be related to emission rates. The method was described in Section 5, and the results of one stripping test were presented earlier in this section. Besides volatility, environmental conditions such as soil temperature, soil moisture content and relative humidity contributed to these variations.

Monitoring of volatiles in the field was continued on 4/19, 5/9 and 6/19, 1983. The last application on the plots was on 11/17/82. On 5/9 and 6/19, 1983 a higher rate of emission was observed (Table B.1, Appendix B) than on 12/20/82. This could be due to higher soil mois-

TABLE 6.23. MEAN AND STANDARD DEVIATION OF TOTAL AMOUNT OF SLUDGE APPLIED AND TOTAL VOLATILE LOSS

Effective Date (1982)	Plot #	Nominal Loading Rate	Weight Sludge Applied, kg (six appl.)	Mean/ APP	Std. Dev.	Weight Oil Applied	Total Volatile Loss/kg	Mean/ APP	Std. Dev.
7/13-12/20	4	3	305	50	8.0	214	32.2	5.37	1.65
7/20-12/20	7	6	519	104	15.9	375	37.7	7.53	3.04
7/13-12/20	5	10	1126	188	43.7	781	52.6	8.76	3.11
7/19-12/20	6	13	1422	237	21.6	1065	52.4	8.74	2.73
7/20-12/20	6	13	1422	237	21.6	1065	52.5	8.75	2.73
Totals			4794	163		3500	227.4	7.84	

APP = Application

ture content and elevated temperatures in May-June 1983 than in December 1982.

As previously discussed, the laboratory experiments were conducted in controlled environmental conditions to investigate the effects of loading rate and temperature on the rate of emissions of volatiles. The procedures and conditions for conducting these experiments were discussed in Section 5. Since it was difficult to evaluate statistically the effects of relative humidity and soil moisture content from field data because of insufficient data for those two parameters, two separate studies, one with high soil moisture content (23 percent) and the other with high relative humidity (75 percent), were performed in the laboratory. The soil temperatures for both tests were held constant at 60°F. One loading rate (6 percent) was tested with high soil moisture content, while two different loading rates (6 and 10 percent) were studied with high relative humidity.

The calculated rates of emissions for laboratory experiments are presented in Table B.2, Appendix B. From these data using the same methodology as for field data recorded in Table 6.21, the data in Table 6.24 were generated. Based on these data, the effects of loading rate, soil temperature, relative humidity, soil moisture content and tilling on emissions were determined.

The Effect of Loading Rate on Emissions

Three different loading rates (3, 6 and 10 percent) were examined in the laboratory at three temperature ranges. The results from laboratory experiments confirmed the field results; i.e., higher mass emission was achieved at higher loading rates. The relationship between emission rates and different loading rates of sludge is shown in Figures 6.5, 6.10 and 6.11. From

TOTAL 6.24. TOTAL VOLATILE LOSS FROM LABORATORY EXPERIMENT

Date of Appl.	Loading Rate (%)	Soil Temp. (°F)	Soil Moist. Content (%)	Relative Humidity (%)	No. of Tilling	Amt.* Sludge Applied (kg)	Amt.** Oil Applied (kg)	Total Loss in 2-hr. (kg)	Total Loss in 1-d (kg)	Total Loss in 7-d (kg)	Max Emission Rate g/hour
3/31/83	3	35	12	52	2	41.746	26.30	.243	.90	2.35	204.762
5/16/83	3	60	12	52	2	41.746	26.30	.335	1.10	2.50	307.144
6/1/83	3	85	12	52	2	41.746	26.30	.350	1.30	4.15	511.906
4/4/83	6	35	12	52	2	82.040	51.68	.330	1.00	2.75	307.143
5/17/83	6	60	12	52	2	82.040	51.68	.367	1.40	3.90	375.397
6/1/83	6	85	12	52	2	82.040	51.68	.388	1.90	5.60	546.033
4/1/83	10	35	12	52	2	133.960	84.39	.433	1.15	3.15	238.889
5/24/83	10	60	12	52	2	133.960	84.39	.473	2.65	5.60	375.397
6/3/83	10	83	12	52	2	133.960	84.39	.622	2.90	7.00	580.160
6/10/83	6	60	23	52	2	82.04	51.68	.550	2.40	7.60	511.906
7/5/83	6	60	12	70	2	82.04	51.68	.300	.80	2.30	341.270
7/5/83	10	60	12	70	2	133.96	84.39	.400	1.50	3.50	341.270

* Volatility of sludge was 8.5% and density of sludge was .90 g/ml

** Amount of oil based on the 63% oil in sludge determined by Extraction Method

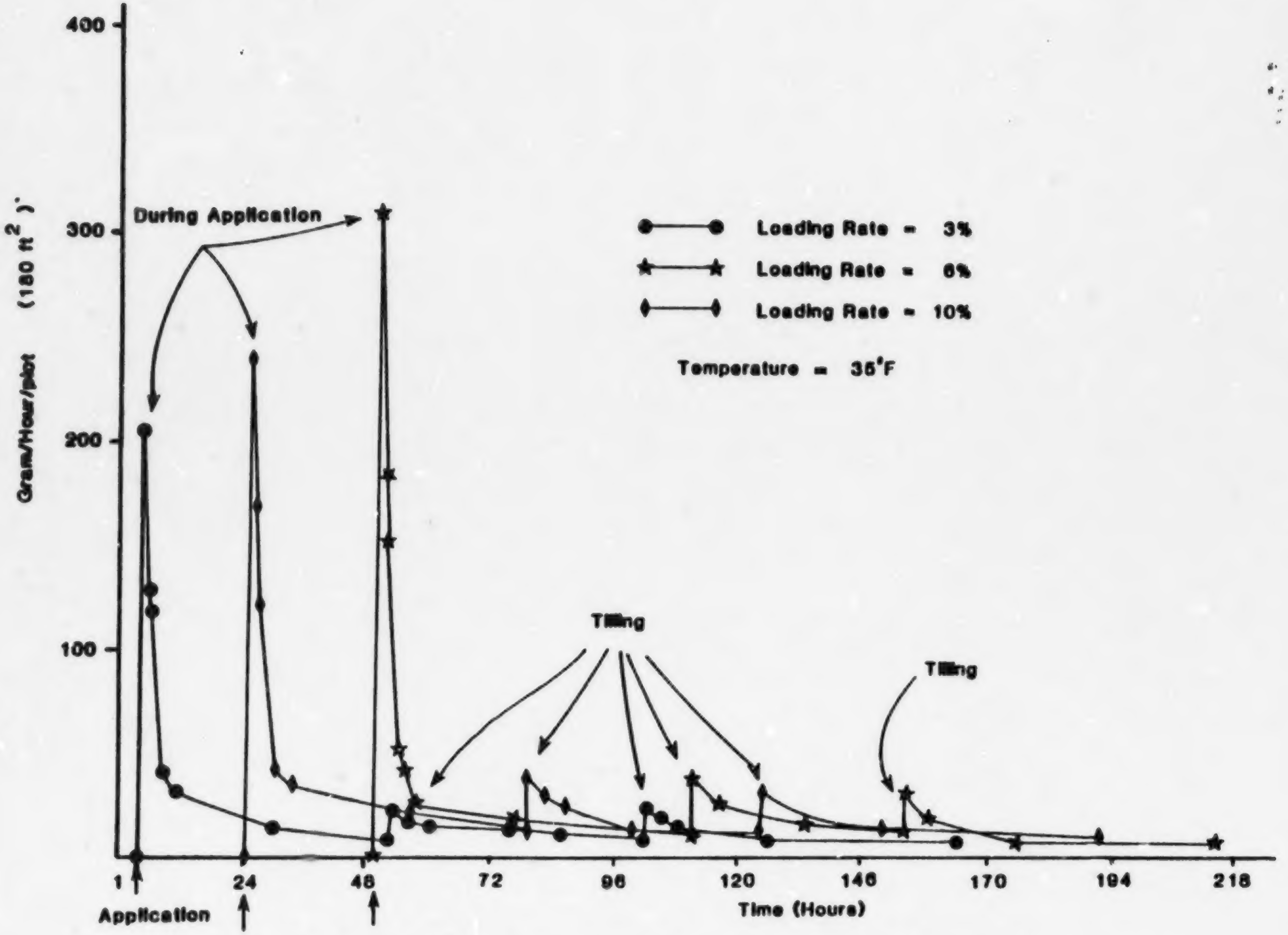

Figure 6.10. The effect of loading rate and tilling frequency on emission in laboratory experiments at 35°F.

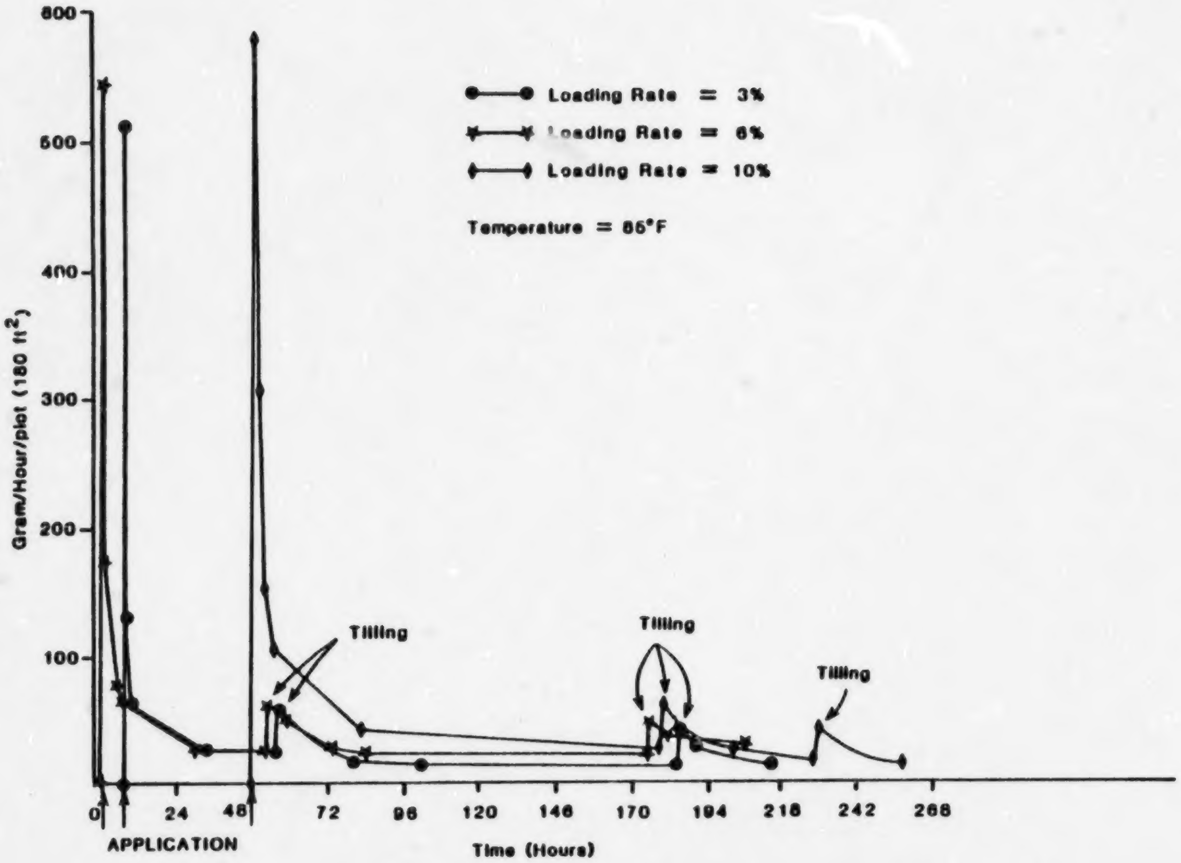

Figure 6.11. The effect of loading rate and tilling frequency on emission in laboratory experiments at 85°F.

these figures and data in Table 6.24, it can be seen that highest emission rate was achieved at 10 percent loading rate for all temperature ranges.

The Effect of Soil Temperature on Emissions

As would be expected, the volatilization rate was strongly affected by temperature changes. The higher the temperature, the higher the vapor pressures of volatile compounds and the greater was the amount of volatiles emitted. Figures 6.12 - 6.14 illustrate the effect of three temperatures (35°F, 60°F, 85°F) at three different loading rates on the rate of emission of volatiles. A trend can be observed for each temperature within one loading rate. Temperature, in addition to its effect on vapor pressure, may also affect such factors as desorption, diffusion to the surface and rates of water loss - all factors that can contribute to the overall rate of loss of volatiles from a soil system. Total seven day loss as a function of variable temperatures and loading rates is shown in Figure 6.15.

Effect of Relative Humidity on Emissions

In all except two experiments, the relative humidity was maintained at 52 percent. Two experiments, one with 6 percent and the other with 10 percent loading rate, were made at 75 percent relative humidity. Soil temperature in these two studies was held at 60°F. The results of these experiments are given in Table B.2, Appendix B and Figure 6.16. As shown in Figure 6.16 there were slight differences in volatilization immediately after sludge application with increased relative humidity. However, later there was a marked decrease in the rate of emission. This is because of the fact that the initial rate of volatile loss of compounds from soil is primarily a function of the concentration of the volatiles at the

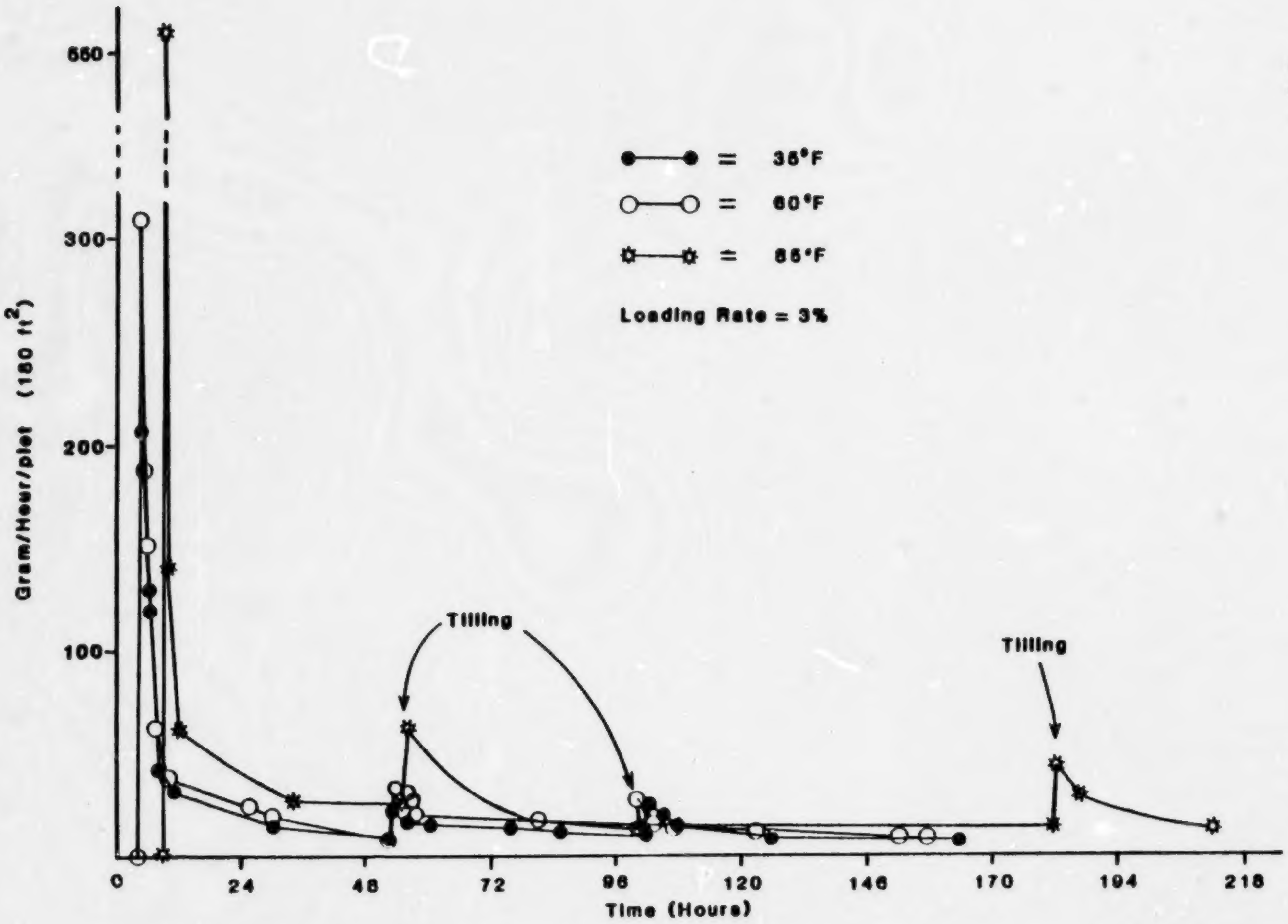

Figure 6.12. The effect of temperature on emission at 3% loading rate.

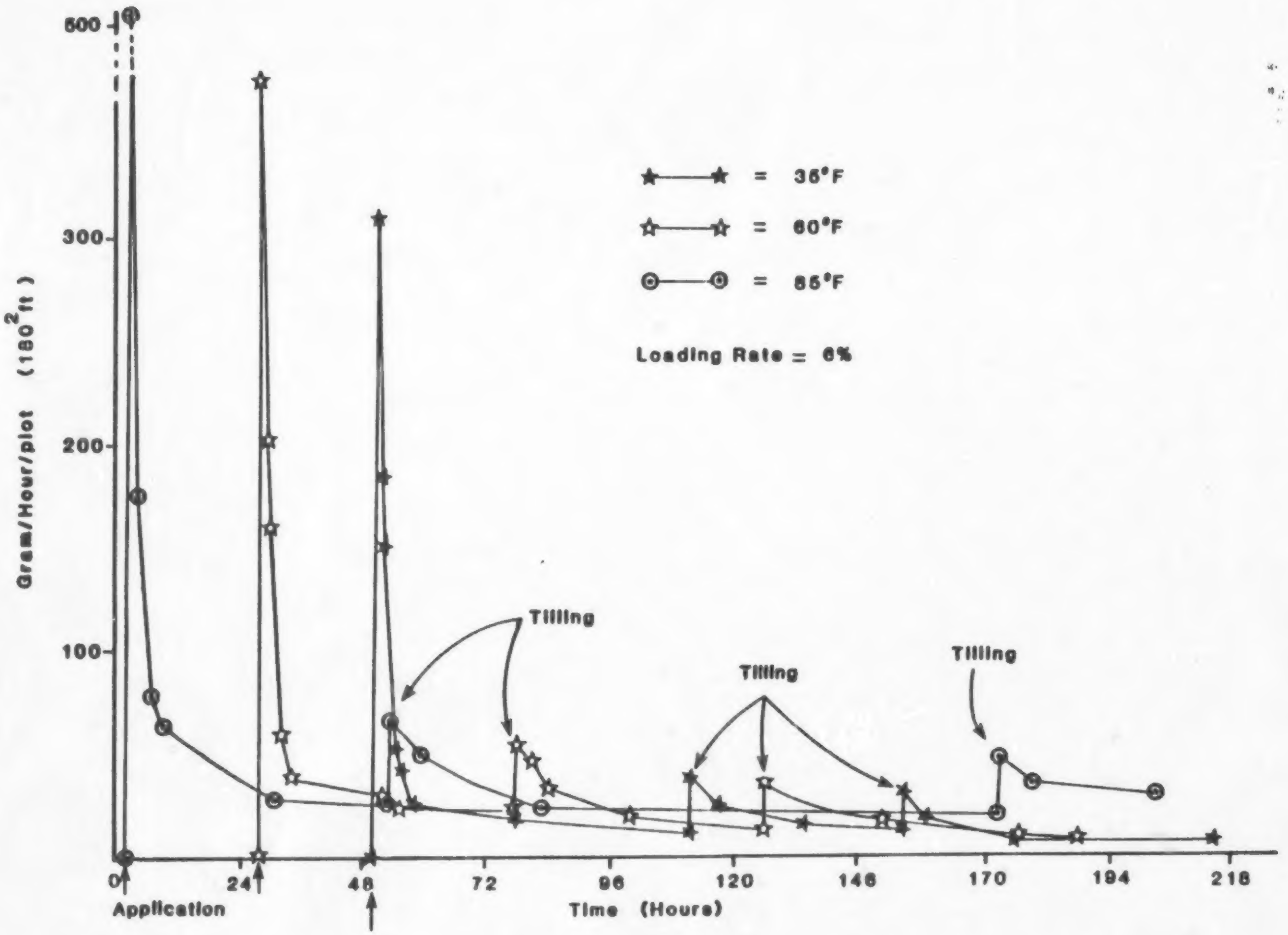

Figure 6.13. The effect of temperature on emission at 6% loading rate.

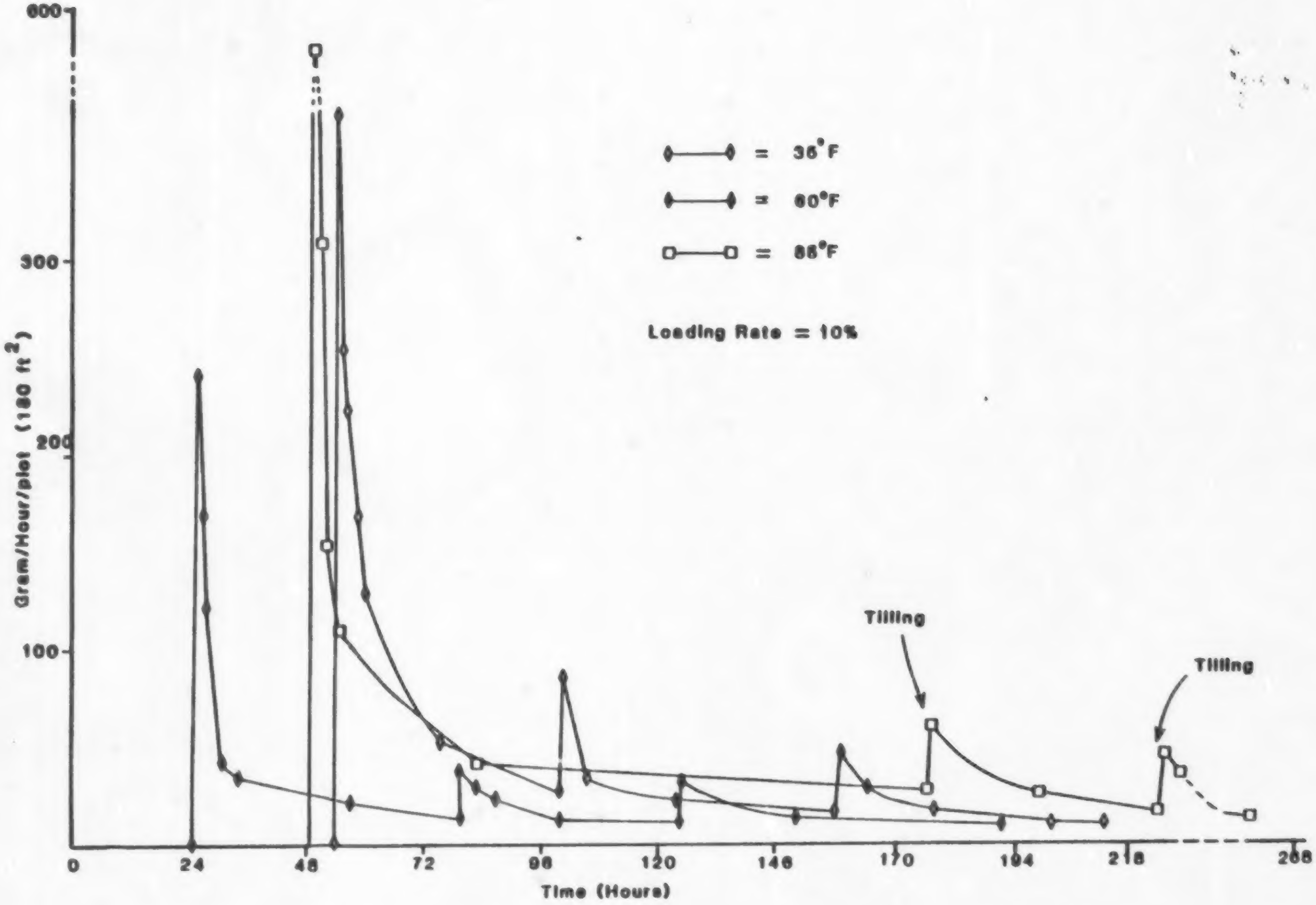

Figure 6.14. The effect of temperature on emission at 10% loading rate.

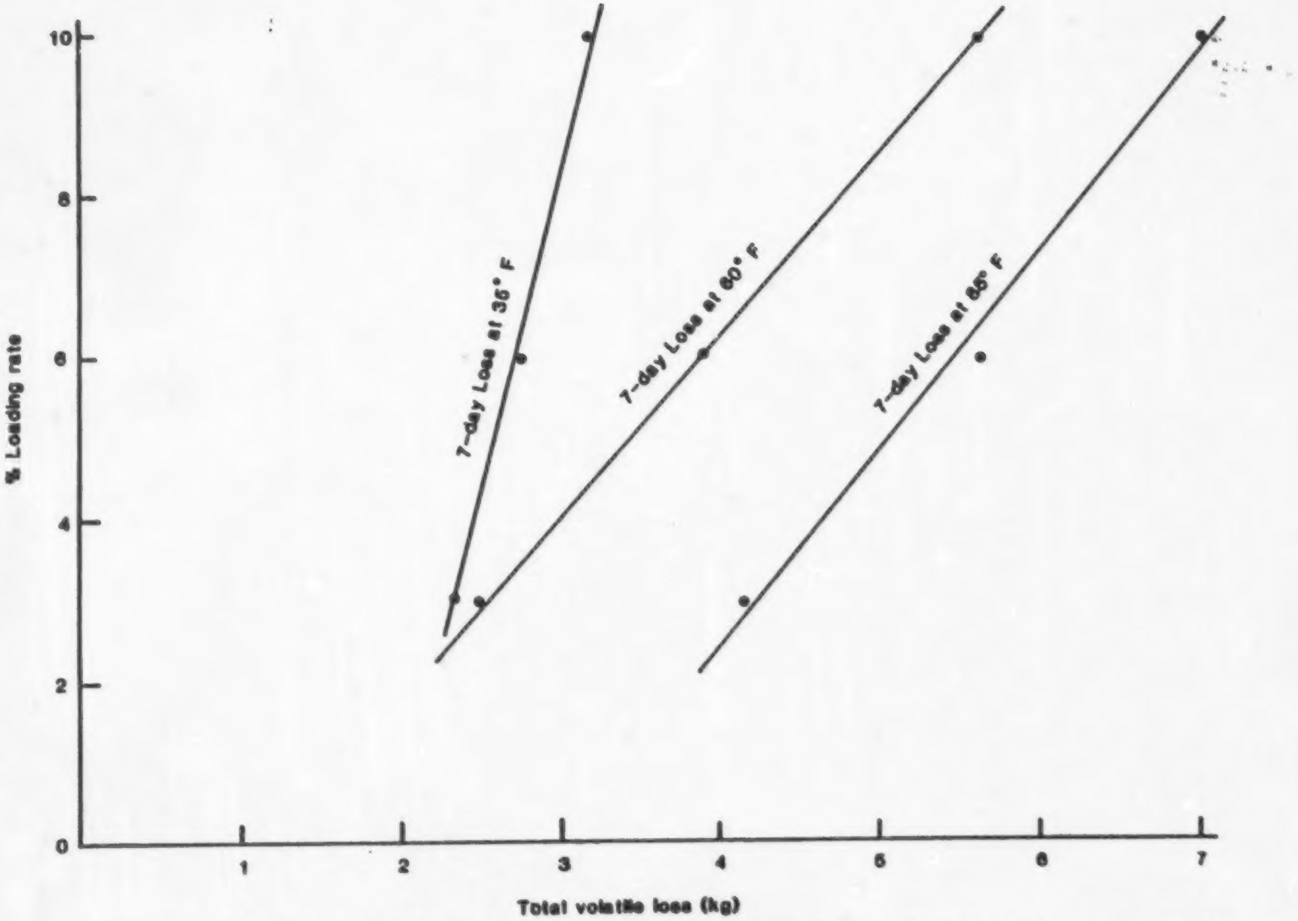

Figure 6.15. Total 7-day loss as a function of variable temperatures and loading rates.

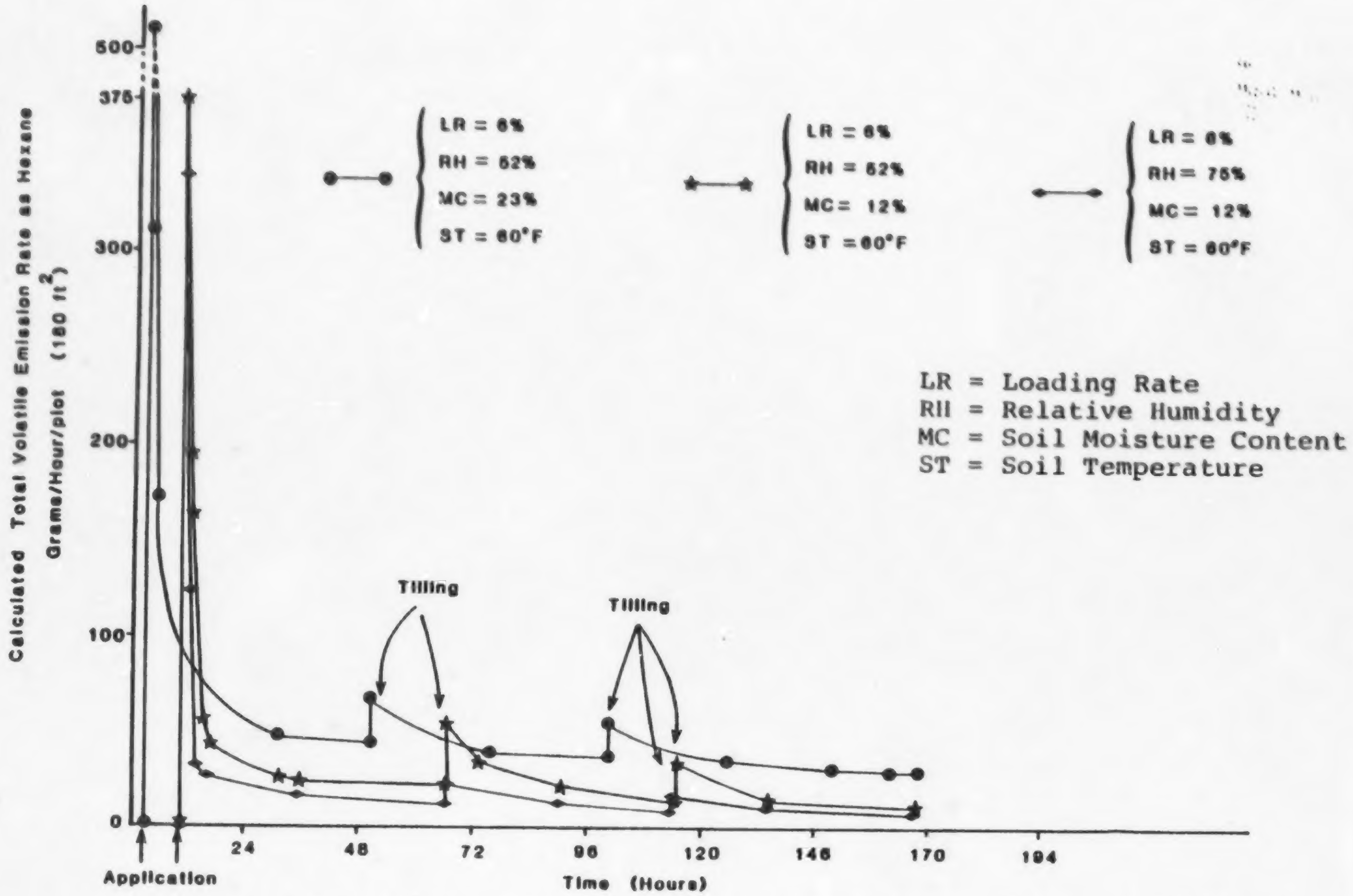

Figure 6.16. The effect of increased relative humidity and moisture content on emission.

surface. Once this initial reservoir is depleted, further loss depends on the rate at which additional chemicals diffuse through the soil column to the surface. Reduction of the humidity means that there is moisture loss from the surface of soil column, and this results in the movement of water to the surface of the soil column which may enhance the rate of migration of the volatiles to the surface; they are then lost by volatilization. Under saturated conditions diffusion occurs at a slow rate through the saturated soil column and under unsaturated conditions compounds volatilize from the soil-oil surface and then diffuse as a gas through the soil atmosphere.

The Effect of Soil Moisture Content on Emissions

All tests but one were run at 12 percent soil moisture content. One test was made at approximately 23 percent by weight soil moisture content. The loading rate and soil moisture were 6 percent and 60°F, respectively. As shown in Figure 6.16 and by the data in Table 6.24, temperature appeared to have a pronounced effect on the emission rate and mass loss. These data (Table 6.24) suggest that as water content increased from 12 percent to 23 percent, the mass loss over a seven day period increased from 3.90 to 7.60 kg. The authors hypothesize that this increase was due to water saturation of the soil particle surfaces, thereby rendering the surfaces unavailable for the compounds. The wetter soil surface was much less permeable to the liquids in the sludge than the dry surface.

THE EFFECT OF TILLING ON THE RATE OF EMISSIONS

In the field the plots were tilled to ensure aerobic conditions for soil microorganisms and to enhance the biodegradation rate. To evaluate tilling effect on emission in the laboratory, the soil and sludge mixture was tilled two times, first on day three and then on day five after application. It was found that tilling initially increased the amount of volatilization for short periods of time. Over a given time period, the emission rate was higher when tilling occurred at the end of the time period, than if frequent tilling occurred during the time period. The concentration after tilling was observed to be at least two times greater than before tilling. It was also observed that the increase in volatilization due to the first tilling was greater than that due to the second and subsequent tillings. The effect of tilling is illustrated clearly in Figures 6.4, 6.5, 6.9-6.12 and 6.16.

STATISTICAL ANALYSIS OF DATA AND DEVELOPMENT OF MODEL

Data was analyzed for the purpose of constructing a 'model'. This model was to relate emission rate mathematically to variables such as soil temperature, soil moisture content, relative humidity and sludge loading rate.

The Statistical Analysis System (SAS) computer package was used to determine the significance of each variable. Within that package multiple linear regression model was used to process the data. By this procedure, the parameters of the model were estimated on the basis of least-squares regression. For any multiple linear model, least-squares minimizes the residual sum of squares and provides an unbiased, linear estimate with minimum variance of parameters (Wallis, 1968).

After the model was constructed by estimating the parameters of the regression line, the parameters were tested to make sure that they were significantly different from zero (Draper and Smith, 1976). The t-test was used to determine the significance of each of the coefficients. F-test was also used to determine the significance of the entire regression equation through the analysis of variance.

The backward elimination method and the coefficient of multiple correlation (R^2) were also used to select the best set of independent variables in the model by utilizing the following variables: loading rate, soil temperature, soil moisture content, relative humidity and time since application. In the backward elimination method the deletion of an independent variable is based on the result of an overall and partial F-test. The R^2 value is also calculated in each step and compared to each other. Finally, residual analyses were performed to provide information as to whether or not the suggested model meets the basic assumption of the regression technique (Draper and Smith, 1976).

An attempt was made to analyze field data and develop an appropriate model from these data. Nevertheless, while several sets of regression trials were made, the results were unacceptable. The effects of relative humidity and soil moisture content could not be evaluated and an appropriate model including all variables could not be developed. Therefore, regression analysis was made only on laboratory data (see Table B.2, Appendix B).

Besides the previously mentioned variables, an attempt was made to include in the model such variables as time since application, inverse of time (1/t) and several combinations of these variables. However, only loading rate, soil temperature, soil moisture content, relative humidity and time since application were found to affect significantly the emission rate. The others were screened out by utilizing backward elimination method, F-test and t-test.

The form of equation used in this study is as follows:

$$Y = \beta_o + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_5X_5 + e$$

where:

Y = emission rate [g/hr],

β_o = intercept of X on Y axis [g/hr],

X_1 = percent loading rate [%],

X_2 = soil temperature [°F],

X_3 = soil moisture content [%],

X_4 = relative humidity [%],

X_5 = time since application

β_i = (i=1-5) regression coefficients which weigh the independent variables as their importance [g/hr - % or g/hr - °F],

e = residual term [g/hr].

The model was first used in one step using the time from starting of application until the end of the test. The model found had an F-ratio of 17.51, and t-test showed the coefficients of all independent variables except relative humidity to be significantly different from zero. Nevertheless, the coefficient of determination (R^2) was only .44.

In an attempt to increase the value of the coefficient of determination (R^2), including all five variables in the model and fulfilling the basic assumption of the regression analysis, analyses were made in two steps:

1. time <10 hours in which rapid decline of emission was observed.
2. time >10 hours in which slow decline of emission was noted.

After several trials utilizing the new approach, the following two models were found to be the best of several:

Model I

Time <10 hours,

$$Y = 76.594 + 9.985X_1 + .769\ X_2 + 8.828\ X_3 - 2.025X_4 - 20.645\ X_5$$

$$R^2 = .830 \qquad F = 27.49$$

Model II

Time >10 hours,

$$Y = .184 + .931\ X_1 + .268\ X_2 + 1.879\ X_3 - .371\ X_4 - .084\ X_5$$

$$R^2 = .766 \qquad F = 49.83$$

Table B.1, in Appendix B, presents the detailed information for both models.

Both Models I and II are found to be significant from a statistical standpoint. Coefficient of determination (R^2) and F-ratios, are high and standard error of estimate in either model is low. Further, the signs of all regression coefficients in both models are correct. Also, the individual t-test for the regression coefficients (Table B.1, Appendix B) show a high degree of significance for the variables in the model. Negative signs for time since application and relative humidity show that these variables inversely affect the rate of emission of volatiles.

To check the validity of the basic assumption of the regression line, (linearity of the regression function, the constancy of the error variance, and the independency and normality of the error terms), residual analysis was performed. This analysis did not show any reason to assume that there was violation of the basic assumption. Thus, these models were chosen for predictive purposes.

SIGNIFICANCE OF RESULTS FROM STANDPOINT OF AIR POLLUTION

The land treatment of petroleum sludge is a potential source of air pollution. To check the significance, the results are compared to National Air Quality Standards (CFR, Nov. 25, 1972). The primary and secondary standards for hydrocarbon for a 3-hour average in time was set 160 $\mu g/m^3$ in 1971 which was changed to 240 $\mu g/m^3$ in 1979.

To obtain pollution concentration on the land treatment area, the "box model" was used. In this model the equilibrium concentration, C_e at a point a distance s from the upwind edge of the land treatment area is:

$$C_e = \frac{ys}{uz}$$

where:

y = rate of emission per unit time per unit area ($g/hr/m^2$) determined from statistical models developed in this study
s = length of the box, lies in the direction of the mean wind
u = average annual wind velocity in Oklahoma City
z = height of the box (average mixing height in Oklahoma City)

Oil was applied to only one acre each day over a 10 day period before the sequence was repeated. For the purpose of this study the following assumptions were made:

A total land treatment area of 10 acres was assumed.

s = 4046.868 = 63.615 (area was assumed to be square)
u = 6.69 meters/sec (13 mph) in Oklahoma City
z_1 = 400 m, mean annual morning mixing height in Oklahoma City
z_2 = 1350 m, mean annual afternoon mixing height in Oklahoma City

Furthermore, the following assumptions were made to determine the rate of emission from statistical models developed in this study:

soil moisture content = 15%
soil temperature = 77°F
relative humidity = 65%
loading rate = 6%
time since application = 1.5 hours
volatility of sludge = 8.5%

Statistical Model I was used to calculate the emission rate from the last acre, 1.5 hours after application, and Model II was used to determine the emission rate from nine single previous applications for the other nine acres. The equilibrium concentration was calculated on the 10th day for each acre using the Box model. The mean annual morning mixing height was used in this calculation. Table 6.25 presents the rate of emission and equilibrium concentration of hydrocarbons after sludge application from each single acre.

Assuming that pollutants were completely mixed over a 4 hectare(10 acre) site, the equilibrium concentration above the total land treatment area was estimated 136 $\mu g/m^3$ which is lower than Ambient Air Quality Standard (240 $\mu g/m^3$). If all of the 10 acres are applied in one day within 3-hours, the equilibrium concentration was estimated 206.8 $\mu g/m^3$ which is also below standard level.

Assuming loading rate of 10 percent, and all the other conditions remaining the same, the equilibrium concentration was estimated 166.72 $\mu g/m^3$ which is again below the standard level.

Therefore, based on the above information, properly designed and managed land treatment systems of petroleum sludge does not cause air pollution problems. If the process is operated properly, there is no need for a buffer zone unless the sludge is highly volatile (>14%),

TABLE 6.25. RATE OF EMISSION AND EQUILIBRIUM CONCENTRATION OF HYDROCARBONS AFTER SLUDGE APPLICATION

Days After Application	Acre No.	Y = Rate of Emission (g/hr/m^2)	C_e = Equilibrium Concentration (µg/m^3)
.0625 = 1.5 hr	10	9.90	65.39
1	9	1.69	11.10
2	8	1.57	10.32
3	7	1.45	9.50
4	6	1.32	8.70
5	5	1.21	7.90
6	4	1.09	7.20
7	3	.97	6.40
8	2	.85	5.60
9	1	.72	4.70
		Total	136.81

temperature and soil moisture content are high or loading rate is greater than 10 percent. Under these conditions it is preferable to apply (against the wind-ward direction) in the afternoon when mixing height is higher than in the morning.

ANALYSIS OF GAS CHROMATOGRAPHIC DATA

As previously discussed in Section 5, the air samples collected over sludge-laden plots were analyzed by gas chromatography (GC) using a flame ionization detector. Because of GC malfunctioning while conducting field studies, most of the samples collected from the field plots and some of the data were discarded. However, later, after the GC problems were resolved, many samples were taken from laboratory experiments and analyzed at appropriate times.

Of the volatile hydrocarbons identified, only fourteen were quantified. These target compounds along with their vapor pressures at 35°F, 60°F and 85°F and their boiling points are presented in Table 6.26 according to increasing boiling points or decreasing vapor pressures. Besides these compounds, other compounds such as propanol, 2-propanone, 2-butanone, 2-pentanone, cyclohexanol, ethylcyclopentane, 2-methyl-1-pentanol and 1,1-Dimethylcyclopentane, were identified by GC-MS in the RSKERL laboratory in Ada, Oklahoma.

Tables B.1 through B.9 in Appendix B summarize data on all of the pollutants measured during the nine laboratory studies. The data in these tables are grouped according to three different temperatures and three different loading rates. In addition, Table B.14 presents data from field experiments.

Much of the information in Tables B.4 through B.14 is self-explanatory, so only salient observations will be

TABLE 6.26. BOILING POINTS AND VAPOR PRESSURES OF MEASURED COMPOUNDS

Compound Name	Boiling Point °F	Vapor Pressure mm/Hg		
		35°F	60°F	85°F
Pentane	36.1	199.52	334.96	562.34
Cyclopentane	49.2	112.20	199.53	398.10
Hexane	69	47.32	94.41	177.82
Methylcyclopentane	72	47.32	94.41	177.82
Benzene	80.1	28.11	63.10	117.48
2,4-Dimethylpentane	80.5	31.62	63.10	117.48
Cyclohexane	80.7	26.61	53.09	112.20
3-Methylhexane	91.85	17.78	35.48	70.79
Methylcyclohexane	100.9	12.59	26.61	50.11
2,5-Dimethylhexane	109	6.68	14.96	31.62
2,3,4-Trimethylpentane	113.467	6.68	14.96	31.62
3-Methylheptane	118.925	4.47	10.59	23.71
2,2,5-Trimethylhexane	124.084	4.47	10.00	19.95
1,4-Dimethylbenzene	138.351	1.496	3.98	10.00

made here.

The above mentioned tables provide information on emission rates at different times since sludge application, at three temperatures, at three loading rates and due to tilling. Included in the tables are total emission rates of the fourteen compounds at each time with the corresponding total volatile emission rates measured as hexane. In addition, the percentage ratio of the fourteen hydrocarbons from GC analyses to the total volatile hydrocarbons measured at the same time with TLV Sniffer is presented.

Figure 6.17 shows the time relationship between emission and loading rate at 85°F for benzene, and Figure 6.18 demonstrates the relationship of emission rates and temperature at 10% loading rate for benzene. Also Figures B.1 through B.16 in Appendix B illustrate the time-concentration curves for other compounds.

It is clear from these figures that the rate of emission of each hydrocarbon increased with increasing temperature and loading rate. For exact emission rates see Tables B.4 through B.13 in Appendix B.

Tables B.4 through B.14 in Appendix B show that compounds having low boiling points and high vapor pressures, such as pentane, cyclopentane, methylcyclopentane and hexane, had lower emission rates than high boiling point and low vapor pressure compounds. This may possibly be related to the fact that high vapor pressure hydrocarbons have already been vaporized during transportation and storage of sludge.

The higher emission rates were found among the hydrocarbons with boiling point ranges from 70 to 119°C. Among these hydrocarbons 2,3,4-Trimethylpentane, with a boiling point of 113.467°C, had the highest rate. The next highest rates pertained to 2,4-Dimethylpentane and

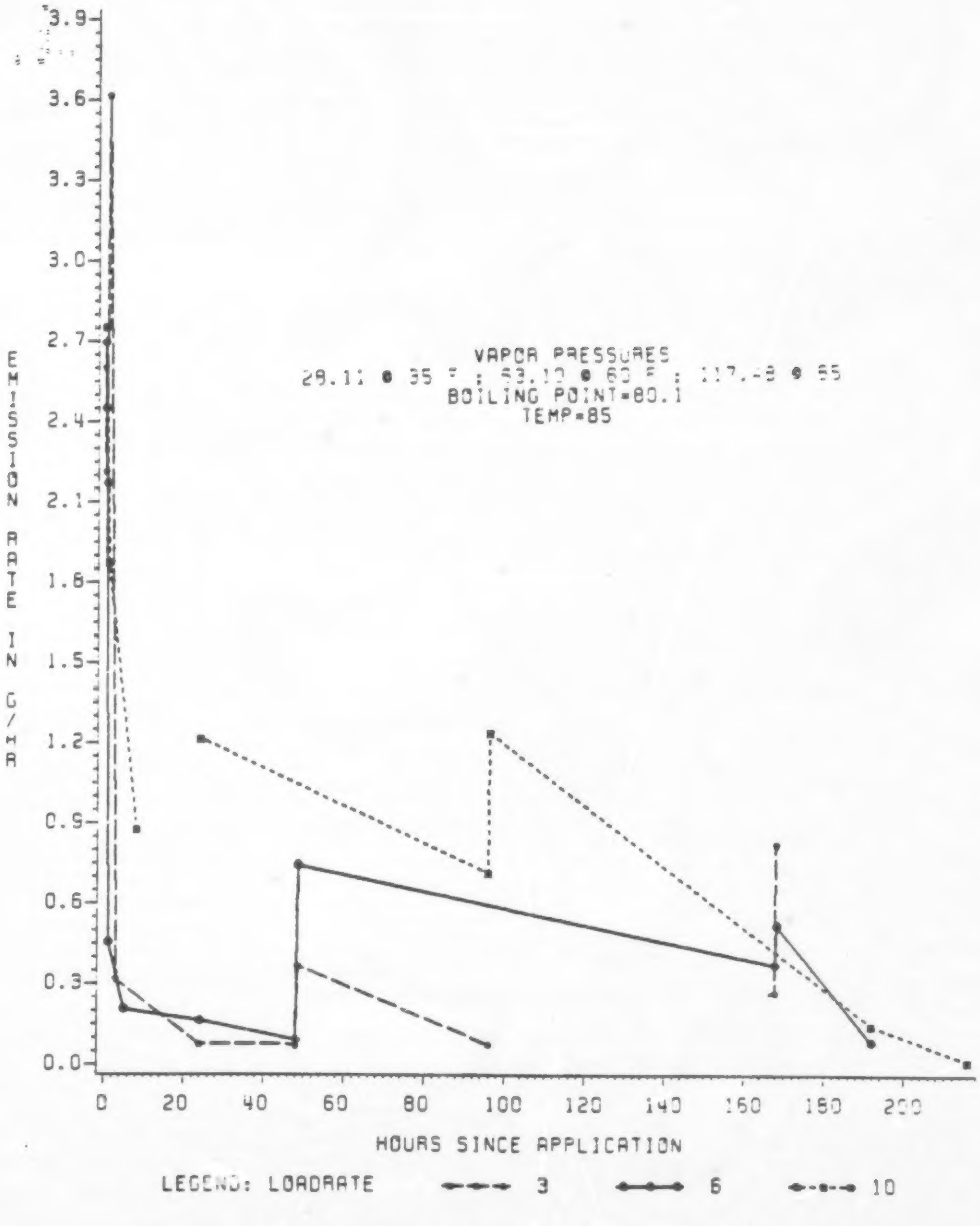

Figure 6.17. Time relation of emission rate and loading rate-Benzene.

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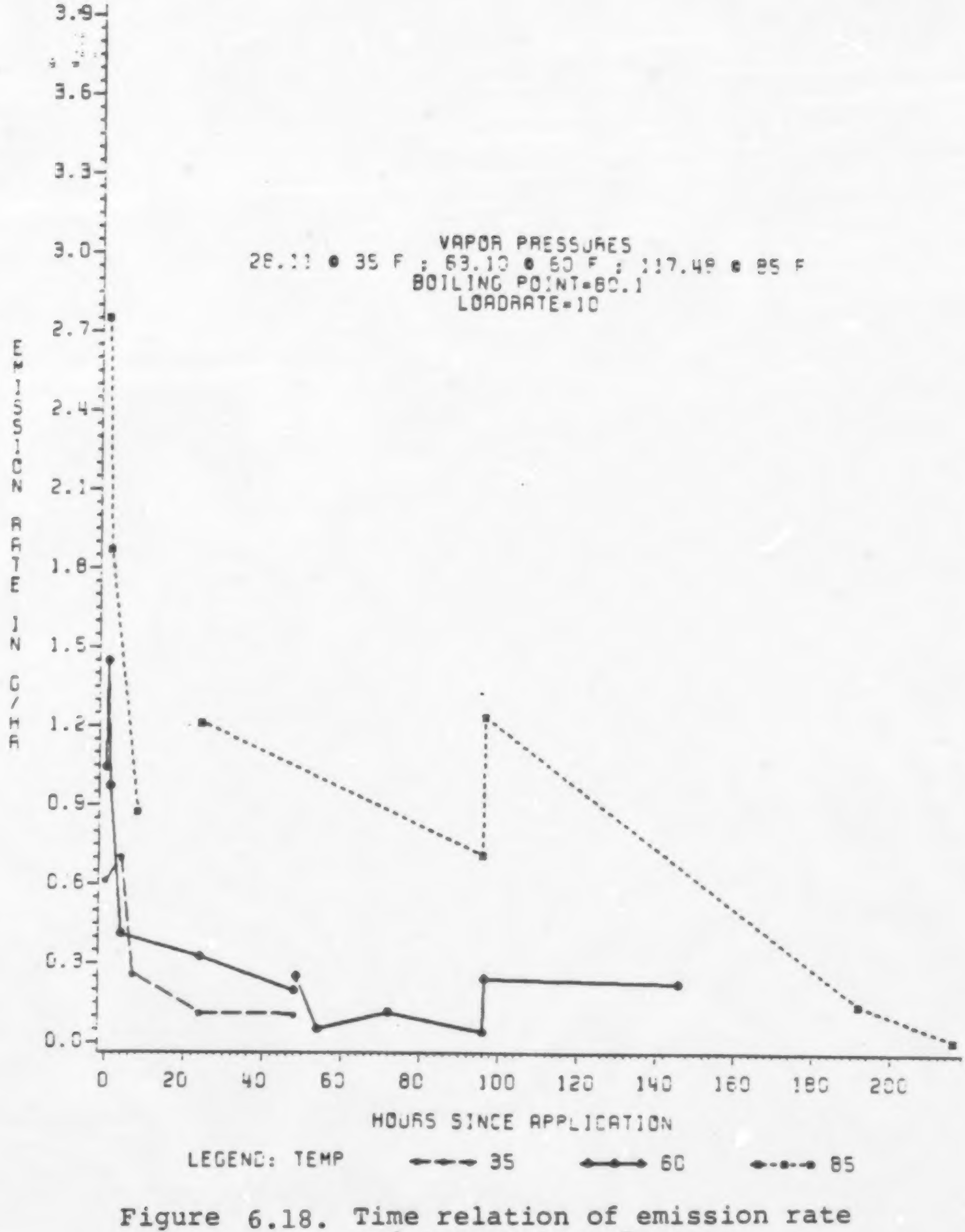

Figure 6.18. Time relation of emission rate and temperature-Benzene.

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3-Methylheptane, respectively.

It was observed that the emission rates of all hydrocarbons decreased with time (Figures 6.17 and 6.18). In some cases, the opposite trends were seen (cyclopentane and pentane); the emission rate was low immediately after application, and it increased for 10 to 60 minutes, and decreased, thereafter, and then followed the pattern of other compounds.

It was further found that, in general, the hydrocarbons identified immediately after sludge application were also identified several months later, but their relative emission rates were much lower.

It is clear from Tables B.1 through B.9 and corresponding figures that tilling increased the release rate of each compound. Figures 6.19 and 6.20 show before- and after-tilling concentrations of each compound. Air samples which produced these chromatograms were taken from plot 4 on April 1983, which had received sludge on November 17, 1982.

FATE OF PRIORITY POLLUTANTS

The fate of priority pollutants present in oily sludge disposed of on land has not been extensively studied. Therefore, one of the objectives of this study was to determine the movement, loss, and degradation of the priority pollutants identified in the applied residues. The zone of incorporation, (the unsaturated zone below this zone) was analyzed for priority pollutants. The results are presented in this section.

The priority pollutants found in the sludge applied (Batches I and II) are presented in Tables 6.27 and 6.28 and the results of the monitoring priority pollutants are presented in Tables 6.29 and 6.30.

From the analysis of these results several observa-

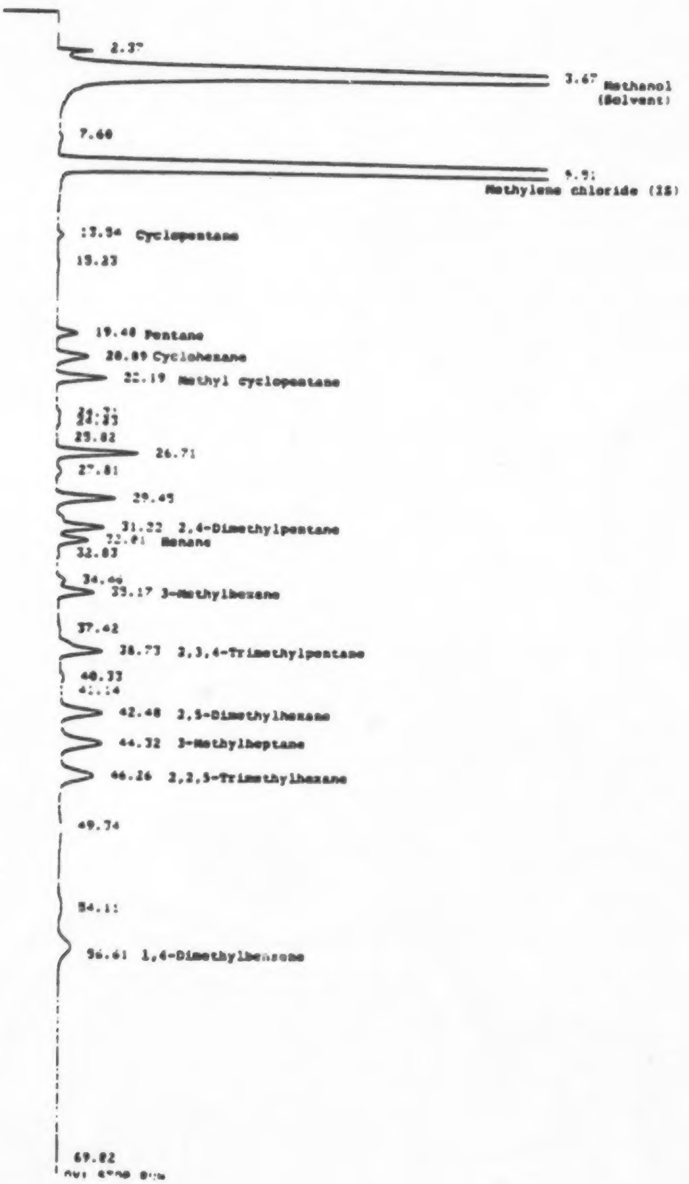

Figure 6.19. Chromatogram of air sample taken from plot 4 (before tilling).

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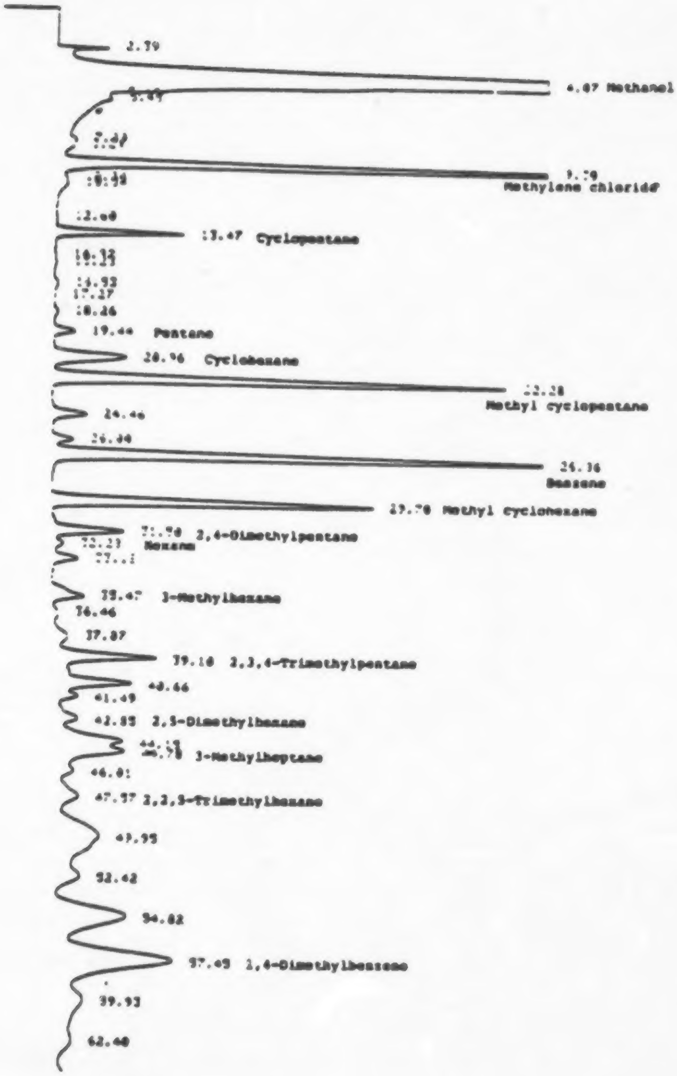

Figure 6.20. Chromatogram of air sample taken from plot 4 (after tilling).

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TABLE 6.27. PRIORITY POLLUTANTS PRESENT IN THE OILY RESIDUES, BATCH I

Names of Compounds	Range of Conc. in ppb
Napthalene	1.61 - 136.61
N-nitrosodiphenylamine	3.4×10^{-4} - 0.075
Isophorone	T - 39.76
Fluorene	T - 1.64
Phenanthrene	2.83×10^{-3} - 0.896
Anthracene	1.13×10^{-4} - 0.574
Pyrene	4.04×10^{-5} - 0.056
Chrysene	T
Benzo(A)anthracene	T
2,4-Dinitrotoluene	0.087 - 630.66
Trichloroethylene	0.047 - 137.70
Benzene	T - 16.83
Ethylbenzene	7.51 - 90.9

Note: T denotes trace amounts less than 10^{-5} ppb.

TABLE 6.28. PRIORITY POLLUTANTS PRESENT IN THE OILY RESIDUES, BATCH II

Compound Present	Conc. in ppb
Toluene	3.5330
Ethylbenzene	0.3740
Isophorone	0.0004

TABLE 6.29. PRIORITY POLLUTANTS PRESENT AT DIFFERENT TIMES FOR PLOT NO. 30

	Concentration Range in ppb				
Compounds	4/7/82 Set I	9/10/82 Set II	9/26/82 Set III	11/8/82 Set IV	12/20/82-6/9/83 Set V - VI
Isophorone	10.74-68.0	0.064-1.299	-	-	None Present
Fluorene	10.21-30.35	-	-	-	
Phenanthrene	0.088-126.4	-	-	-	
Anthracene	0.002-0.021	-	-	-	
Trichloroethylene	1.98-2.67	-	0.514-0.762	-	
Benzene	T - 0.0011	T - 0.0037	-	0.0010	
Ethylbenzene	T - 0.0017	-	-	-	
Nitrobenzene	-	0.019-0.038	-	-	
Phenol	-	T - 0.00019	-	-	
2-Nitrophenol	-	T	-	-	
Pentachlorophenol	-	0.0007	-	-	
Pyrene	-	-	T	-	

Note: T denotes trace amounts less than 10^{-5} ppb

TABLE 6.30. PRIORITY POLLUTANTS PRESENT AT DIFFERENT TIMES FOR PLOT NO. 35

Compounds	Concentration Range in ppb 6/7/82 Set I	9/10/82 Set II	9/26/82 Set III	11/8/82 - 6/9/83 Set IV - V
Isophorone	0.728-14.7	T	-	None Present
Phenanthrene	0.004-522,98	-	-	
Anthracene	0.002-0.267	-	-	
Fluoranthene	0.006-0.065	-	-	
2,4-Dinitrotoluene	0.41-3.62	-	1.572	
Benzene	0.0002-0.0004	-	-	
Phenol	-	0.0001-.0009	-	
Pyrene	-	-	0.0001-0.0002	

Note: T indicates trace amounts less than 10^{-5} ppb tions have been made:

1) The initial concentrations of organic compounds were in the ppb range.
2) The concentrations of the compounds decreased with time.
3) The number of compounds decreased with time.
4) The 2nd batch of oily residue obtained did not have as many pollutants as the 1st batch.
5) After a period of 426 days the priority pollutant concentrations were below the detection limit of the extraction and analytical procedures.
6) Initially there were no phenolic compounds present in the sludges, but after a period of 387 days there were phenolics present. This leads to the conclusion that they were formed in the soil matrix.

On combining the results of the zone of incorporation and the unsaturated zone monitoring, it can be said that there were no contamination problems in terms of priority pollutants. It appears that, since the concentration of the compounds were very low in the sludges and also there were no compounds present in the unsaturated zones the most probable 'fate' of these compounds was volatilization or degradation.

UNSATURATED ZONE MONITORING

The results of the unsaturated zone monitoring on plots 30 and 35 for priority pollutants are presented in Table 6.31. It can be seen from the data that not as many compounds were identified in the site soil as were present in the sludge, and that over a 15 month period, the concentration of priority pollutants decreased below the detection limits of the extraction and analytical

TABLE 6.31. ORGANIC PRIORITY POLLUTANTS FOUND IN THE UNSATURATED ZONE

Plot No./Date of Sampling	Compounds Present	Range of Conc. in ppb
30, 4/7/82	*Chloroform	T - 12.09
	Trichloroethylene	T - 3.48
35, 4/7/82	*Chloroform	T - 103.01
	Trichloroethylene	T - 98.97
	Benzene	T - 1.85×10^3
	Isophorone	T - 0.026
	Phenanthrene	T -
	Anthracene	
	Fluoranthene	T
30, 9/30/82	*Chloroform	26.29 - 65.69
	Trichloroethylene	T - 11.02
	Benzene	T
35, 9/30/82	*Chloroform	0.552 - 57.34
	Trichloroethylene	T - 1.853
30, 35 7/15/83	None present	-

Note: T indicates trace amounts less than 0.1 ppb

* Chloroform appears to be a contaminant, since it was also present in the blanks.

procedures. These results indicate that no significant movement of priority pollutants into the soil of the unsaturated zone, below the zone of incorporation (30 cm), (11.8 in) occurred over the 15 month period.

FATE OF METALS IN SOIL

As a part of the evaluation of land treatment, the concentration of metals in the soil was monitored periodically. The concentration of selected metals in the site soil before application of any residues was determined and compared to the concentration of the same metals in the soil at different times during the project.

Table 6.32 lists the concentration of metals in the site soil before application of residues. The values listed are means from at least 21 different samples analyzed from the site. Table 6.33 lists the metal concentrations in the applied oil. Tables 6.34 through 6.37 list metals concentrations in different plots, showing how the concentrations varied over time.

As can be seen from Table 6.32, the background soil contained low metal concentrations. The applied sludge also contained low metal concentrations, as shown in Table 6.33.

No definite trends in metal concentration buildup could be identified for the metals except for Cr and Zn. Chromium and zinc did show an increase in concentration in the soil which was significant at $\alpha = 0.05$. This increase occurred in all plots. No significant increase in the concentration of Cu, Ni, Pb or Cd occurred between 8/21/81 and 6/9/83, the first date of application and the final analysis date, respectively.

The theoretical amount of the metals which should be present in the soil was determined by calculating the amount of metal applied in the sludge, and adding the

TABLE 6.32. BACKGROUND METAL CONCENTRATIONS IN SITE SOIL

Element	Conc. (mg/kg)*
Cu	10.1
Cr	12.2
Zn	29.7
Ni	22.0
Pb	14.7
Cd	<0.5

[*] Mean of at least 21 values.

TABLE 6.33. METALS IN APPLIED OIL (mg/kg)

Batch No.	Zn	Ni	Cu	Pb	Cr	Cd
1	12.97	22.20	1.00	2.00	<0.2	0.25
2	25.49	12.57	0.47	1.12	1.65	<0.50
3	349.42	10.96	6.69	22.31	23.24	16.04
4	210.26	9.32	7.21	10.41	12.53	10.32

TABLE 6.34. CONC. OF METALS IN PLOT 8

Metal	Conc. (mg/kg)		
	Bkg.	11/17/82	6/9/83
Cu	10.1	23.5	9.8
Cr	12.2	24.0	23.3
Zn	29.7	35.0	83.3
Ni	22.0	20.0	15.9
Pb	14.7	24.0	14.3
Cd	<0.5	-	2.0

TABLE 6.35. CONC. OF METALS IN PLOT 13

Metal	Conc. (mg/kg)			
	Bkg.	11/17/82	12/20/82	6/9/83
Cu	10.1	22.0	18.0	10.1
Cr	12.2	17.7	22.0	26.6
Zn	29.7	33.7	53.0	48.3
Ni	22.0	16.3	15.0	12.3
Pb	14.7	16.0	17.0	17.0
Cd	<0.5	<0.5	<0.5	1.0

TABLE 6.36. CONC. OF METALS IN PLOT 20

Metal	Conc. (mg/kg)		
	Bkg.	11/17/82	6/9/83
Cu	10.1	59.0	13.9
Cr	12.2	15.7	25.6
Zn	29.7	38.7	45.7
Ni	22.0	15.7	15.7
Pb	14.7	16.0	12.7
Cd	<0.5	<0.5	<0.5

TABLE 6.37. CONC. OF METALS IN PLOT 26

Metal	Conc. (mg/kg)			
	Bkg.	11/17/82	12/20/82	6/9/83
Cu	10.1	22.5	22.5	9.7
Cr	12.2	22.0	18.0	23.7
Zn	29.7	14.5	-	49.7
Ni	22.0	14.5	16.5	18.0
Pb	14.7	14.0	19.0	13.0
Cd	<0.5	<0.5	1.3	0.5

background concentration of the metal present in the soil to this value. These theoretical concentrations were then compared to the values obtained by analyzing the site soil at the end of the project. There was a reasonably good agreement between the two sets of values, except for chromium, where the theoretical values were appreciably lower than the measured values. The data for this comparison is presented in Table 6.38.

No significant buildup of metals occurred during the project period. Zinc and chromium were present at levels significantly above background, but the absolute values were still very low. Table 6.40 shows accepted metal concentrations which can be tolerated in the soil as a result of irrigation or other activities. If the metal concentrations in the plot with the highest loading rate are considered - 27 percent over 22 months - the useful life of the plot would be limited by the zinc and cadmium concentrations. Using the values in Table 6.40, the cadmium concentration in the soil would reach the critical level in 24 years, and the zinc concentration in 17 years. Thus, if sludges with the concentrations of metals given in Table 6.33 were applied, the life expectancy of the site would be 17 years.

Soil samples from below the zone of incorporation were also analyzed for metals, to determine if any migration of metals had taken place. There was no significant increase in the metal concentration below the zone of incorporation. Table 6.39 shows the results of deep core analysis. Raw metal data is presented in Appendix C.

MODELING AND DESIGN OF LAND TREATMENT SYSTEMS

Several recommendations relevant to process modeling

TABLE 6.38. COMPARISONS OF METAL CONC. PRESENT IN SOIL WITH AMOUNT APPLIED

Plot No.	Total Oil Applied[(1)] (%)	Metal Conc. Applied[(2)] (mg/kg)	Metal Conc. Present[(3)] (mg/kg)
Zinc			
Bkg.	-	-	35.15
13	9.2	44.28	48.25
21	22.4	70.51	69.00
8	26.8	72.36	83.25
20	14.3	46.60	45.70
26	12.0	46.67	37.00
Nickel			
Bkg.	-	-	22.92
13	9.2	25.04	12.25
21	22.4	70.51	69.00
8	26.8	29.04	15.00
20	14.3	26.26	15.70
26	12.0	25.77	14.50
Copper			
Bkg.	-	-	12.00
13	9.2	12.27	10.13
21	22.4	12.80	9.67
8	26.8	12.88	9.75
20	14.3	12.29	13.90
26	12.0	12.37	13.00
Lead			
Bkg.	-	-	14.66
13	9.2	15.22	17.00
21	22.4	17.13	16.67
8	26.8	17.31	14.25
20	14.3	15.54	12.70
26	12.0	15.44	14.00

(continued)

TABLE 6.38. (continued)

Plot No.	Total Oil Applied(1) (%)	Metal Conc. Applied(2) (mg/kg)	Metal Conc. Present(3) (mg/kg)
Chromium			
Bkg.	-	-	13.60
13	9.2	14.13	26.23
21	22.4	15.80	25.67
8	26.8	15.88	23.25
20	14.3	17.26	25.60
26	12.0	14.25	22.00
Cadmium			
Bkg.	-	-	<0.50
13	9.2	0.74	1.00
21	22.4	1.93	1.83
8	26.8	2.00	2.00
20	14.3	0.79	<0.50
26	12.0	0.84	<0.50

(1) Total oil applied to plot during the project on a dry weight basis.

(2) Theoretical conc. of metal in soil based on amount applied plus background.

(3) Conc. of metals in soil at end of project by analysis.

TABLE 6.39. METAL CONCENTRATION IN DEEP CORES (mg/kg)

Metal	Depth (cm)	Plot No./% Oil Applied		
		#30/16.1	#35/17.7	#21/22.4
Cd	91 - 107	<.50	<.50	<.50
	152 - 168	.50	.50	.50
	91 - 107	29.50	31.00	28.00
Cr	152 - 168	36.00	29.00	34.83
	91 - 107	17.00	15.00	14.00
Cu	152 - 168	16.00	25.00	23.60
	91 - 107	29.00	24.00	23.25
Ni	152 - 168	36.50	34.00	31.80
	91 - 107	22.50	14.00	21.63
Pb	152 - 168	28.50	21.50	18.40
	91 - 107	40.50	42.50	37.38
Zn	152 - 168	37.50	43.00	42.70
Cu	0 - 30	5.5	9.5	9.0
	30 - 61	11.8	14.0	9.0
	61 - 91	32.0	14.0	11.5
Ni	0 - 30	12.0	10.5	12.5
	30 - 61	21.8	16.5	10.0
	61 - 91	28.0	19.0	15.5
Zn	0 - 30	35.5	46.0	47.3
	30 - 61	41.0	49.5	40.0
	61 - 91	52.0	52.0	43.0
Pb	0 - 30	7.0	19.0	12.5
	30 - 61	7.0	13.0	18.0
	61 - 91	11.0	15.0	17.5
Cd	0 - 30	0.5	<0.5	0.5
	30 - 61	0.5	0.5	<0.5
	61 - 91	0.5	0.5	0.5
Cr	0 - 30	15.5	30.0	22.0
	30 - 61	24.8	35.5	32.0
	61 - 91	32.5	34.0	30.5

TABLE 6.40. ACCEPTED METAL CONCENTRATIONS IN SOIL AS A RESULT OF IRRIGATION OR OTHER ACTIVITIES

Element	Concentration (mg/kg)
As	500
Cd	20
Co	500
Cr	1,000
Cu	250
Ni	100
Pb	1,000
Zn	500

Brown (1980)

and design were made based on data presented in the preceding subsections. Although overall oil losses increase with increasing loading rates and decreasing loading frequencies, there is a practical limit above which operational consideration such as ability to operate cultivation equipment and control runoff became limiting factors.

A maximum hydraulic loading for this research site based on existing field conditions was found to be approximately 40 l/m^2 (1 gal/ft^2). At the oil concentrations of the sludges used in this study (60 - 90 percent) the maximum hydraulic loading corresponds to approximately 7 percent dwb in terms of the increase in oil concentration in a 30 cm depth zone of incorporation. Though higher loadings were in fact made, operational problems such as those described above inevitably resulted.

It must be noted that the duration of the study period was not long enough for the systems to approach equilibrium. Therefore, the maximum hydraulic loading of 40 l/m^2 per application will probably not be attainable when the system reaches equilibrium. Depending upon the final equilibrium concentration and the oil concentration of the sludge a hydraulic loading to achieve an oil content per application of 3 - 4 percent dwb is an achievable goal. Except for very low sludge oil concentrations in which the long-term hydraulic loading (and not the single application) becomes the limiting constraint, annual oil loading rate could be maintained for low oil content sludges by increasing the number of applications.

It is suggested that, from a practical standpoint, physical site conditions are the primary determinative controlling loading rates and, therefore, loss rates in an oily waste land treatment system. Therefore, the authors predict that in any properly operated system, treating API Separator sludges from petroleum refineries loss rates equivalent to those found in this study would be expected.

Oily waste land treatment systems should be designed for 'equilibrium conditions'. For the purpose of this discussion, equilibrium is reached when the amount of degradable material applied is removed (via degradation and volatilization) in the period prior to the next application. This definition is somewhat oversimplified, since the concentrations and loss rates for degradable waste fractions are in reality dynamic due to a combination of factors. Therefore, 'equilibrium' applies to time intervals over which sufficient loading/loss cycles have occurred such that process fluctuations are insignificant. This approach ignores the possible buildup of refractory organics and inorganics which may be produced in the process or be present in the waste sludge. Certainly these are important considerations. The build up of refractory compounds was not found to be a significant problem in this study, however, equilibrium conditions were not achieved.

Though it was shown that the various oily fractions are removed from the zone of incorporation at different rates, the metabolic pathways and biochemical interrelationships are not sufficiently understood to warrant the use of a multiple-substrate process model. Thus, a pseudo single-substrate model was developed. Continuing monitoring would support or reject the validity of this simplifying assumption. The use of a single substrate model had distinct advantages. Measurement of the major process control parameter, substrate concentration, is made easier if fractionation of the recovered oil is not required.

Determination of a composite overall rate coefficient also makes the design methodology more applicable to a variety of oily substrates. It is recognized that the coefficient is not constant but a function of many factors. However, in the design methodology discussed below the coefficient has been assumed constant. The results of these investigations of oil loss kinetics indicate that a first-order biodegradation rate constant of 0.003 day^{-1} is reasonable for the API Separator sludge used in this study. Based on the first-order reaction kinetics a simplified process model was developed. The following general assumptions apply:

1) Single component substrate (oil).
2) Constant first-order rate coefficient.
3) Application rate and frequency held constant.

If, at equilibrium, the amount of substrate added, L_a, is equal to the amount degraded, $(L_o - L_t)$, then the following first-order relationships are valid:

$$L_t = L_o \, e^{-Kt}$$

$$\begin{aligned} L_a &= L_o - L_t \\ &= L_o - L_o \, e^{-Kt} \\ &= L_o \, (1 - e^{Kt}) \end{aligned}$$

And therefore,

$$L_o = \frac{L_a}{(1 - e^{-Kt})}$$

is an expression for the maximum equilibrium concentration, where 't' is the (constant) time between applications of L_a. With L_o known, the number of cycles 'n' required to reach equilibrium may be found from the equation:

$$L_o = L_a \sum_{i-o}^{n} e^{-Kti}$$

If equilibrium is arbitrarily defined as having been reached when L_o of the 'nth' cycle is within some percentage of the theoretical maximum L_o, then the above equation may be easily solved for 'n' by iteration.

Table 6.41 presents a matrix of equilibrium values for combinations of loading rate and loading frequency (LR/LF) which bracket anticipated practical loading possibilities. A value of first-order rate coefficient of 0.003 day^{-1} was used in the calculations. Equilibrium was reached when an increase in maximum concentration was less than 1 percent of the previous maximum. If a constant loading rate and loading frequency were used the system would require four to five years to reach equilibrium.

In addition to the maximum and minimum equilibrium concentrations and the number of cycles required to reach equilibrium, the time required after cessation of applications to reduce the substrate concentration to 2 percent dwb was computed. The value of 2 percent oil in soil was arbitrarily selected as a milestone corresponding to site closure, and cessation of active land treatment operations. During the subsequent post-closure period the soil could be revegetated if the oil concentration was less than 2 percent and toxics are not present above the inhibition concentration.

As expected, the higher loading rates required somewhat longer periods to reach equilibrium, with the higher ultimate equilibrium concentrations than lower loading rates. Increasing loading frequency reduced the time to equilibrium and the maximum concentrations, but raised the minimum equilibrium concentrations.

In order to evaluate the relative effects of changes in rate coefficients on equilibrium concentrations, values of 0.001 day^{-1} and 0.005 day^{-1} were applied to the

TABLE 6.41. EQUILIBRIUM VALUES ASSUMING $K = .003$ DAY^{-1}

LR/LF (% dwb)/(year^{-1})	L_a (% dwb)	e^{-Kt}	$L_o$max (dwb)	L_t eq (% dwb)	n	$t_{2\%}$ (days)
12/1	12	.334	18.02	6.02	5	730
12/2	6	.578	14.22	8.22	9	650
12/4	3	.761	12.55	9.55	17	610
12/6	2	.833	11.98	9.98	25	600
12/12	1	.913	11.49	10.49	47	580
9/1	9	.334	13.51	4.51	4	640
9/2	4.5	.578	10.66	6.16	8	560
9/4	2.25	.761	9.41	7.16	16	520
9/6	1.5	.833	8.98	7.48	24	500
6/1	6	.334	9.01	3.01	4	500
6/1	3	.578	7.11	4.11	8	420
6/4	1.5	.761	6.27	4.77	15	380
6/6	1	.833	5.00	4.99	23	370

TABLE 6.42. EQUILIBRIUM VALUES ASSUMING OTHER RATE COEFFICIENTS

LR/LF (% dwb)/(year^{-1})	L_a (% dwb)	e^{-Kt}	$L_o$max (dwb)	L_t eq (% dwb)	n	$t_{2\%}$ (days)
K = .005 days^{-1}						
9/1	9	.161	10.73	1.73	3	340
9/2	4.5	.402	7.53	3.03	5	270
9/4	2.25	.634	6.15	3.90	9	230
9/6	1.5	.738	5.73	4.23	15	210
K = .001 Days^{-1}						
9/1	9	.694	29.41	20.41	12	2690
9/2	4.5	.833	26.94	22.44	24	2600
9/4	2.25	.912	25.57	23.32	47	2550
9/6	1.5	.941	25.42	23.92	70	2540

annual loading rate of 9 percent (Table 6.42). Dramatic increases in both equilibrium concentration and time required to reach equilibrium and degrade to values for post-closure revegetation were seen for this annual loading rate when a K of 0.001 day^{-1} was used in the model. In fact, the minimum equilibrium concentration at this loading is above what could be operationally maintained. Substantial decreases in the equilibrium values resulted when a K of 0.005 day^{-1} was used.

As an alternative to the relatively slow build-up of soil oil concentration when constant LR/LF is used, a more rapid initial increase in soil oil concentration could be achieved by a few heavy applications followed by lower constant loading rates. There are several advantages and disadvantages to these two alternative start-up strategies. The rapid start-up approach would be more advantageous for refineries which have existing quantities sludge stored in lagoons or holding tanks. Substantial temporary storage is available in the zone of incorporation which would facilitate conversion from existing storage-type disposal to land treatment. The disadvantage to heavy initial application is the potential for problems associated with massive initial slug loads of oil and other constituents to the system. Note that the equilibrium condition corresponds to the condition of lowest operability, since the oil content of the soil is highest.

As with any biological waste treatment system, the development of a population of acclimated microorganisms is critical to the success of the process. Though acclimation of the system did not appear to be a problem in this study, the lack of reliable data in the initial phases of the project did not allow acclimation to be adequately assessed.

Advantages to the slow start-up approach would be greatest for those refineries which have existing sludge treatment and/or disposal systems. Redirection of an existing steady state waste stream to a land treatment site is essentially all that would be required for conversion to the system. Low initial sludge loadings would also build in a certain factor of safety, in that early monitoring of the system would allow changes in the design loading rates prior to a build-up to unacceptably high levels. Determination and refinement of the biokinetic constants would also be possible with the slow start-up approach. The potential for build-up of refractory organics and inorganics could be assessed prior to reaching unacceptably high concentrations, and the planned design life of the systems modified accordingly.

It is highly recommended that initial soil testing and pilot studies be conducted prior to design and construction of an oily waste land treatment system. Testing the mechanical characteristics of potential site soils both before and after oily sludge addition in the laboratory is critical in order to estimate important characteristics of the soil during system operation.

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APPENDIX A

OIL LOADING AND CONTENT DATA

TABLE A.1. OIL LOADING DATA

Plot	Date	Elapsed Time	Percent Applied*
1	82181	0	1.25
	11982	151	2.50
	71982	332	2.93
	81782	361	2.93
	90982	384	2.93
	100482	409	-
	101482	419	2.50
	110282	438	2.50
	111782	453	2.50
2	82181	0	0.83
	11982	151	1.25
	30882	199	1.25
	71382	326	1.25
	81782	361	1.25
	92382	398	0.29
	92382	398	-
	101482	419	2.20
	101482	419	-
	111782	453	1.25
	122082	486	1.25
4	82181	0	0.29
	12082	152	0.58
	71382	326	0.58
	81282	356	0.58
	92382	398	0.58
	101282	417	0.41
	110282	438	0.58
	111782	453	0.58
5	82181	0	0.86
	12082	152	1.92
	71382	326	1.92
	81282	356	1.92
	92382	398	1.92
	101282	417	1.92
	110282	438	2.50
	111782	453	1.92

(continued)

TABLE A.1. (continued)

Plot	Date	Elapsed Time	Percent Applied*
6	82181	0	1.25
	11982	151	2.50
	41582	237	2.50
	71982	332	2.93
	81782	361	2.93
	91082	385	2.93
	101482	419	2.50
	111782	453	2.50
7	82181	0	0.48
	11982	151	1.15
	42082	252	1.15
	72082	333	1.15
	81782	361	1.15
	92382	398	1.15
	92382	398	-
	101282	417	1.15
	111782	453	1.15
8	82181	0	7.48
	11982	151	11.55
	111782	453	7.75
9	82181	0	0.32
	12082	152	0.58
	30882	199	0.58
	71382	326	0.58
	81282	356	0.58
	92382	398	0.58
	110282	438	0.58
	111782	453	0.58
	122082	486	0.58
10	82181	0	0.96
	12082	152	3.45
	72082	333	3.45
	110982	445	6.90
11	82181	0	0.48
	11982	151	1.15
	71982	332	1.15
	81782	361	1.15
	91082	385	1.15
	101282	417	1.15
	110282	434	1.15
	111782	453	1.15

(continued)

TABLE A.1. (continued)

Plot	Date	Elapsed Time	Percent Applied*
13	82181	0	0.58
	12082	152	0.96
	30882	199	0.96
	42082	252	0.96
	72082	333	0.96
	81282	356	0.96
	92382	398	0.96
	92382	398	-
	101282	417	0.96
	111782	453	0.96
	122082	486	0.96
14	82182	0	0.29
	12082	152	0.58
	71382	332	0.58
	81282	356	0.58
	92382	398	0.58
	101282	417	0.58
	110282	438	0.58
	111782	453	0.58
15	82181	0	0.96
	12082	152	3.45
	71382	332	3.45
	110982	445	6.90
16	82181	0	3.90
	11982	151	3.00
	111782	453	3.45
17	82181	0	3.45
	11982	151	3.45
	111782	453	1.73
18	82181	0	0.19
	11982	151	0.29
	30992	199	0.29
	71382	326	0.29
	81282	356	0.29
	92382	398	0.29
	101282	417	0.29
	110282	438	0.29
	111782	453	0.29
	122082	486	0.29

TABLE A.1. (continued)

Plot	Date	Elapsed Time	Percent Applied*
20	82181	0	0.86
	10282	152	1.92
	41582	247	1.92
	72082	333	1.92
	81282	356	1.92
	92382	398	1.92
	101282	417	1.92
	111782	453	1.92
21	82181	0	7.48
	11982	151	7.42
	111782	453	7.48
22	82181	0	5.18
	11982	151	11.50
	111782	453	5.75
23	82181	0	2.49
	12082	152	7.48
	72082	333	7.48
	122082	486	4.23
24	82181	0	0.58
	12082	152	1.73
	71382	332	1.73
	110982	445	3.45
25	82181	0	0.20
	12082	152	0.29
	30882	199	0.29
	41582	247	0.29
	72082	333	0.29
	81282	356	0.29
	92382	398	0.29
	101282	417	0.29
26	82181	0	0.83
	11982	151	1.25
	30882	199	1.25
	42282	254	1.25
	71982	332	1.25
	81782	361	1.25
	91082	385	1.25
	101282	417	1.25
	111782	453	1.25
	122082	486	1.25

(continued)

TABLE A.1. (continued)

Plot	Date	Elapsed Time	Percent Applied*
28	82181	0	1.73
	12082	152	5.75
	72082	333	5.75
	110982	445	11.50
29	82181	0	1.73
	12082	152	3.52
	72082	333	5.75
	110982	445	11.50
30	82181	0	5.75
	12082	152	6.90
	122082	486	3.45
31	82181	0	3.45
	11982	151	3.45
	111782	453	1.73
32	82181	0	0.32
	11982	151	0.58
	30882	199	0.58
	42082	252	0.58
	81782	361	0.58
	92382	398	0.58
	92382	398	-
	101482	419	0.58
	111782	453	0.58
	122082	486	0.58
34	82181	0	0.58
	11982	151	0.96
	30882	199	0.96
	41582	237	0.96
	71382	326	0.96
	81282	356	0.96
	92382	398	0.96
	101482	419	0.96
	122082	486	0.96
35	82181	0	5.18
	12082	152	6.81
	122082	486	5.75

(continued)

TABLE A.1. (continued)

Plot	Date	Elapsed Time	Percent Applied*
36	82181	0	2.49
	11982	151	6.09
	71982	332	4.04
	122082	486	3.97
38	82181	0	0.58
	12082	152	1.73
	71382	326	1.73
	110982	445	3.45

* in % dry weight basis

TABLE A.2. SOIL SOIL CONTENT DATA

Plot	Oil Content	Date
1	9.47	60983
	11.16	60983
	11.83	60983
	12.92	111782
	12.00	111782
	12.58	111782
	12.26	101482
	12.48	101482
	11.96	101482
	9.55	100482
	8.71	100482
	9.69	100482
	7.81	90982
	8.07	90982
	7.49	90982
	8.71	81782
	7.81	81782
	4.91	81782
	6.06	81782
	7.93	81782
	5.50	81082
	4.53	81082
	5.08	81082
	4.05	81082
	4.86	81082
2	6.15	60983
	6.97	60983
	7.17	60983
	5.09	122082
	5.07	122082
	4.96	111782
	5.38	111782
	4.96	111782
	4.60	101482
	5.94	101482
	6.39	101482
	2.94	100782
	3.63	100782
	3.51	100782
	3.78	92382
	4.29	92382
	3.62	92382
	3.99	92282

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
2 (con't)	4.15	92282
	3.37	92282
	3.78	90982
	3.78	90982
	4.41	90982
	2.27	81782
	3.28	81782
	3.87	81782
	3.28	81782
	3.54	81782
	1.75	81082
	2.15	81082
	2.23	81082
	1.59	81082
	2.60	81082
3	0.20	60983
	0.18	60983
	0.56	60983
	0.17	60983
	0.26	60983
	0.10	60983
4	1.84	60983
	1.61	60983
	1.42	60983
	1.54	60983
	1.74	60983
	1.59	60983
	2.33	51083
	2.21	51083
	2.21	51083
	1.62	111782
	1.90	111782
	1.71	111782
	1.33	100782
	1.30	100782
	1.30	100782
	1.04	92282
	0.96	92282
	0.94	92282
	1.10	90982
	1.08	90982

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
4 (con't)	1.05	90982
	0.40	81082
	0.41	81082
	0.44	81082
	0.59	81082
	0.50	81082
5	6.77	60983
	7.30	60983
	6.92	60983
	8.11	51083
	8.05	51083
	7.61	51083
	6.91	111782
	6.90	111782
	7.09	111782
	5.12	100782
	4.68	100782
	3.73	100782
	3.58	92282
	3.35	92282
	3.42	92282
	4.02	90982
	3.85	90982
	3.81	90982
	3.86	81782
	4.58	81782
	5.44	81782
	4.39	81782
	4.16	81782
	3.86	81282
	4.58	81282
	5.44	81282
	4.39	81282
	4.16	81282
	1.81	81082
	2.54	81082
	3.16	81082
	1.49	81082
	1.24	81082

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
6	9.68	60983
	15.26	60983
	10.14	60983
	8.13	60983
	8.29	60983
	8.06	60983
	10.59	111782
	10.24	111782
	9.37	111782
	11.92	101482
	11.39	101482
	10.13	101482
	9.32	100482
	9.02	100482
	10.12	100482
	7.98	81782
	12.27	81782
	8.63	81782
	7.80	81782
	8.17	81782
	5.59	81082
	3.07	81082
	5.74	81082
	5.60	81082
	5.74	81082
7	5.08	60983
	4.83	60983
	4.90	60983
	4.76	111782
	4.40	111782
	4.45	111782
	3.71	100782
	3.68	100782
	3.69	100782
	4.24	92382
	4.57	92382
	4.36	92382
	2.82	92282
	2.79	92282
	3.27	92282
	2.73	90982
	3.45	90982
	3.05	90982

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
7 (con't)	3.30	81782
	3.02	81782
	3.07	81782
	3.58	81782
	3.23	81782
	2.02	81082
	1.60	81082
	1.52	81082
	1.54	81082
	1.46	81082
8	6.76	60983
	10.17	60983
	10.61	60983
	8.65	60983
	8.88	60983
	10.09	60983
	6.67	111782
	6.84	111782
	6.81	111782
	7.40	92682
	7.41	92682
	7.09	92682
	8.50	91082
	7.96	91082
	8.09	91082
9	2.96	60983
	3.10	60983
	3.08	60983
	3.78	51083
	3.39	51083
	3.70	51083
	2.71	122082
	3.14	122082
	3.09	122082
	2.45	111782
	2.70	111782
	2.42	111782
	1.93	100782
	2.10	100782
	1.94	100782
	1.50	92282
	1.71	92282

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
9 (con't)	1.56	92282
	1.51	81282
	0.88	81282
	1.48	81282
	1.08	81282
	1.22	81282
	0.89	81082
	0.84	81082
	1.17	81082
	0.79	81082
	1.25	81082
	0.55	81082
	0.70	81082
	0.94	81082
	0.50	81082
	1.08	81082
10	6.41	60983
	6.99	60983
	7.14	60983
	8.30	51083
	8.56	51083
	8.01	51083
	3.30	110882
	3.19	110882
	3.45	110882
	3.36	92682
	3.21	92682
	3.39	92682
	3.74	91082
	3.47	91082
	3.70	91082
11	4.37	60983
	4.42	60983
	4.91	60983
	4.83	111782
	5.14	111782
	4.80	111782
	3.16	100482
	2.96	100482
	3.58	100482
	2.70	90982
	2.45	90982

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
11 (con't)	2.63	90982
	2.95	81782
	2.69	81782
	2.94	81782
	2.79	81782
	2.65	81782
	1.66	81082
	1.39	81082
	1.58	81082
	1.50	81082
	1.67	81082
12	0.10	60983
	0.06	60983
	0.09	60983
13	4.65	60983
	4.76	60983
	4.14	60983
	4.25	122082
	5.21	122082
	4.74	122082
	4.60	111782
	4.94	111782
	4.81	111782
	4.02	100782
	3.92	100782
	3.37	100782
	4.09	92382
	4.30	92382
	4.48	92382
	3.13	92282
	2.88	92282
	3.14	92282
	3.57	90982
	3.47	90982
	3.72	90982
	3.86	81382
	2.66	81382
	4.08	81382
	3.05	81382
	2.11	81082
	1.60	81082
	1.93	81082

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
13 (con't)	2.88	81082
	3.07	81082
14	2.00	60983
	2.21	60983
	2.15	60983
	2.52	51083
	2.69	51083
	2.88	51083
	2.15	111782
	2.07	111782
	2.15	111782
	1.47	100782
	1.32	100782
	1.29	100782
	1.03	92282
	0.97	92282
	1.01	92282
	1.62	90982
	1.39	90982
	1.82	90982
	1.03	81282
	0.75	81282
	1.01	81282
	1.26	81282
	1.24	81282
	0.53	81082
	0.56	81082
	0.63	81082
	0.57	81082
	0.57	81082
15	9.72	60983
	7.98	60983
	7.74	60983
	8.46	51083
	8.45	51083
	8.49	51083
	3.09	110882
	3.20	110882
	3.15	110882
	4.20	92682
	4.16	92682
	3.87	92682

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
15 (con't)	3.99	91082
	3.98	91082
	4.16	91082
16	5.34	60983
	5.51	60983
	5.43	60983
	3.20	111782
	3.31	111782
	3.48	111782
	3.99	92682
	4.01	92682
	4.02	92682
	4.07	91082
	4.12	91082
	4.01	91082
17	2.91	60983
	2.45	60983
	3.16	60983
	1.80	111782
	1.92	111782
	1.77	111782
	2.74	92682
	2.21	92682
	2.31	92682
	2.21	91092
	3.35	91082
	2.70	91082
18	1.27	60983
	1.33	60983
	1.58	60983
	1.83	122082
	1.50	122082
	1.41	122082
	1.46	111782
	1.46	111782
	1.60	111782
	0.96	100782
	1.17	100782
	0.99	100782
	1.13	92282
	1.11	92282

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
18 (con't)	1.05	92282
	1.06	81382
	1.05	81382
	0.89	81382
	0.89	81382
	0.93	81382
	0.17	81082
	0.73	81082
	0.62	81082
	0.25	81082
	0.33	81082
19	0.07	60983
	0.06	60983
	0.04	60983
	0.08	51083
	0.10	51083
	0.92	51083
	1.34	91082
	1.46	91082
	1.29	91082
20	5.70	60983
	5.74	60983
	4.95	60983
	7.22	51083
	6.92	51083
	6.89	51083
	5.98	111782
	6.52	111782
	7.18	111782
	5.18	100782
	5.43	100782
	5.80	100782
	4.55	92282
	4.11	92282
	4.83	92282
	5.30	90982
	4.98	90982
	5.05	90982
	5.97	81782
	6.04	81782
	6.14	81782
	7.22	81782

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
20 (con't)	5.87	81782
	5.97	81282
	6.04	81282
	6.14	81282
	7.22	81282
	5.87	81282
	1.84	81082
	1.21	81082
	0.96	81082
	2.80	81082
	2.14	81082
21	7.54	60983
	6.87	60983
	6.94	60983
	5.96	111782
	4.43	111782
	3.46	111782
	4.72	110982
	4.57	110982
	5.11	110982
	5.31	92682
	5.11	92682
	4.98	92682
	6.67	91082
	5.94	91082
	6.41	91082
22	8.76	60983
	8.60	60983
	8.68	60983
	8.87	60983
	8.21	60983
	8.32	60983
	5.34	111782
	6.20	111782
	5.90	111782
	6.65	92682
	6.49	92682
	6.49	92682
	7.85	91082
	9.38	91082
	8.74	91082

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
23	7.50	60983
	7.39	60983
	4.30	60983
	2.93	122082
	3.70	122082
	2.29	122082
	7.91	110982
	7.85	110982
	8.31	110982
	8.24	92682
	8.42	92682
	8.32	92682
	9.81	91082
	10.02	91082
	9.34	91082
24	7.18	60983
	4.14	60983
	4.13	60983
	4.53	51083
	4.60	51083
	4.53	51083
	4.47	111782
	4.77	111782
	1.76	110882
	1.60	110882
	1.85	110882
	1.90	92682
	2.00	92682
	1.83	92682
	2.79	91082
	2.59	91082
	2.80	91082
25	1.10	60983
	1.32	60983
	1.34	60983
	2.02	51083
	1.90	51083
	1.83	51083
	1.64	111782
	1.52	111782
	1.49	111782
	1.51	100782

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
25 (con't)	1.39	100782
	1.32	100782
	1.72	92382
	1.38	92382
	1.69	92382
	1.19	92282
	1.21	92282
	1.21	92282
	1.38	91082
	1.98	91082
	1.62	91082
	1.47	81782
	1.50	81782
	1.61	81782
	1.39	81782
	1.43	81782
	1.47	81282
	1.50	81282
	1.61	81282
	1.39	81282
	1.43	81282
	0.28	81082
	0.57	81082
	0.66	81082
	0.90	81082
	0.54	81082
26	5.18	60983
	5.18	60983
	4.82	60983
	2.89	122082
	2.65	122082
	5.11	111782
	5.04	111782
	5.36	111782
	3.88	100482
	4.67	100482
	4.77	100482
	4.34	90982
	4.28	90982
	4.00	90982
	4.73	81782
	4.37	81782
	4.49	81782
	4.19	81782
	4.83	81782

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
27	0.11	60983
	0.13	60983
	0.09	60983
28	12.59	60983
	11.53	60983
	9.85	60983
	6.66	110982
	6.43	110982
	6.55	110982
	6.76	92682
	6.46	92682
	6.74	92682
	8.68	91082
	9.16	91082
	7.54	91082
29	10.13	60983
	9.35	60983
	10.46	60983
	10.06	51083
	10.27	51083
	9.11	51083
	4.53	110982
	5.26	110982
	5.14	110982
	5.13	92682
	5.44	92682
	5.90	92682
	5.86	91082
	5.93	91082
	5.59	91082
30	4.97	51083
	6.28	51083
	4.62	51083
	1.91	122082
	2.02	122082
	1.88	122082
	2.67	111782
	2.83	111782
	2.72	111782
	2.90	110882
	2.75	110882
	2.90	110882

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
30 (con't)	3.18	92682
	3.14	92682
	3.13	92682
	4.39	91082
	4.91	91082
	4.19	91082
31	2.12	60983
	1.81	60983
	1.68	60983
	1.61	111782
	1.61	111782
	1.77	111782
	1.84	92682
	1.91	92682
	1.99	92682
	2.31	91082
	1.92	91082
	1.76	91082
32	2.31	60983
	2.11	60983
	2.39	60983
	1.90	122082
	1.80	122082
	1.82	122082
	2.57	111782
	2.16	111782
	2.57	111782
	2.76	101482
	2.87	101482
	2.90	101482
	2.32	100782
	2.03	100782
	2.19	100782
	2.05	100482
	2.25	100482
	3.32	100482
	2.56	92382
	2.80	92382
	2.94	92382
	1.86	92282
	2.15	92282
	2.02	92282
	2.14	90982

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
32 (con't)	2.25	90982
	2.12	90982
	2.36	81782
	2.56	81782
	2.23	81782
	2.32	81782
	2.46	81782
33	0.11	60983
	0.12	60983
	0.11	60983
34	4.04	60983
	4.05	60983
	4.50	60983
	4.20	51083
	4.15	51083
	4.32	51083
	2.83	122082
	3.41	122082
	2.74	122082
	4.77	101482
	4.81	101482
	4.59	101482
	2.74	92282
	2.70	92282
	2.92	92282
	3.11	90982
	3.11	90982
	3.09	90982
	1.71	81282
	2.80	81282
	1.78	81282
	3.17	81282
	3.58	81282
35	6.62	51083
	6.17	51083
	4.69	51083
	2.56	122082
	2.54	122082
	2.33	122082
	3.74	111782
	3.83	111782
	3.40	111782

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
35 (con't)	3.84	110882
	3.82	110882
	3.95	110882
	4.15	92682
	2.45	92682
	2.23	92682
	5.13	91082
	5.36	91082
	5.63	91082
36	8.00	60983
	7.03	60983
	6.94	60983
	3.98	122082
	3.23	122082
	6.39	122082
	8.57	91082
	8.18	91082
	8.52	91082
37	0.08	60983
	0.12	60983
38	4.73	60983
	4.29	60983
	3.32	60983
	2.46	110982
	2.82	110982
	2.67	110982
	3.56	91082
	3.59	91082
	3.35	91082
39	0.06	60983
	0.06	60983
	0.05	51083
	0.05	51083
	0.08	51083
40	0.05	60983
	0.08	60983
	0.04	60983
	0.08	51083
	0.07	51083
	0.06	51083

(continued)

TABLE A.2. (continued)

Plot	Oil Content	Date
41	0.03	60983
	0.03	60983
	0.04	60983
42	1.80	60983
	1.28	60983
	1.77	60983
43	1.33	60983
	1.18	60983
	1.32	60983
44	5.61	60983
	5.67	60983
	5.67	60983
	6.58	51083
	7.29	51083
	6.96	51083
45	6.92	60983
	6.50	60983
	8.15	60983
	9.57	51083
	8.79	51083
	9.03	51083
	0.03	110882
	0.03	110882
	0.05	110882

TABLE A.3. TIME SERIES OIL CONTENT HISTORY

------------------------------ PLOT=1 ------------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	1.25
11982	151	L	.	2.50
71982	332	L	.	2.93
81782	361	L	.	2.93
90982	384	B	7.79	.
90982	384	H	10.72	2.93
100482	409	E	9.61	.
101482	419	J	9.73	.
101482	419	A	12.23	2.50
110282	438	F	.	2.50
111782	453	B	12.50	.
111782	453	H	15.00	2.50
60983	657	E	10.82	.

(continued)

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TABLE A.3. (continued)

----------------------------- PLOT=2 -----------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.831
11982	151	L	.	1.245
30882	199	L	.	1.245
71382	326	L	.	1.245
81782	361	L	.	1.245
90982	384	E	3.99	.
92282	397	B	3.83	.
92382	398	H	4.12	0.290
92382	398	A	3.90	.
100782	412	B	3.57	.
101482	419	H	5.77	2.200
101482	419	A	5.64	.
111782	453	B	5.10	.
111782	453	H	6.34	1.245
122082	486	B	5.08	.
122082	486	H	6.33	1.245
60983	657	E	6.76	.

----------------------------- PLOT=4 -----------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.2875
12082	152	L	.	0.5750
71382	326	L	.	0.5750
81282	356	L	.	0.5750
90982	384	E	1.08	.
92282	397	B	0.98	.
92382	398	H	1.55	0.5750
100782	412	B	1.31	.
101282	417	H	1.71	0.4070
110282	438	F	.	0.575
111782	453	B	1.74	.
111782	453	H	2.32	0.575
51083	627	E	2.25	.
60983	657	E	1.62	.

(continued)

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TABLE A.3. (continued)

PLOT=5

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.863
12082	152	L	.	1.920
71382	326	L	.	1.920
81282	356	L	.	1.920
90982	384	E	3.89	.
92282	397	B	3.45	.
92382	398	H	5.37	1.920
100782	412	B	4.90	.
101282	417	H	6.82	1.920
110282	438	F	.	2.500
111782	453	B	6.97	.
111782	453	H	8.89	1.920
51083	627	E	7.92	.
60983	657	E	7.00	.

PLOT=6

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	1.246
11982	151	L	.	2.500
41582	237	L	.	2.500
71982	332	L	.	2.930
81782	361	L	.	2.930
91082	385	F	.	2.930
100482	409	E	9.49	.
101482	419	J	9.15	.
101482	419	A	11.65	2.500
111782	453	B	10.07	.
111782	453	H	12.57	2.500
60983	657	E	8.16	.

(continued)

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TABLE A.3. (continued)

PLOT=7

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.479
11982	151	L	.	1.150
42082	252	L	.	1.150
72082	333	L	.	1.150
81782	361	L	.	1.150
90982	384	E	3.08	.
92282	397	B	2.80	.
92382	398	H	3.95	1.150
92382	398	A	4.30	.
100782	412	B	3.69	.
101282	417	H	4.84	1.150
111782	453	B	4.54	.
111782	453	H	5.69	1.150
60983	657	E	4.94	.

PLOT=8

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	7.475
11982	151	L	.	11.550
91082	335	E	8.18	.
92582	401	E	7.30	.
111782	453	B	6.77	.
111782	453	H	14.25	7.745
60983	657	E	9.68	.

(continued)

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TABLE ...3. (continued)

PLOT=9

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.319
12082	152	L	.	0.575
30832	199	L	.	0.575
71382	326	L	.	0.575
81282	356	L	.	0.575
92282	397	B	1.59	.
92382	398	H	2.16	0.575
100782	412	B	1.99	.
110282	438	F	.	0.575
111782	453	B	2.52	.
111782	453	H	3.10	0.575
122082	486	B	2.98	.
122082	486	H	3.55	0.575
51083	627	E	3.62	.
60983	657	E	3.05	.

PLOT=10

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.96
12082	152	L	.	3.45
72082	333	L	.	3.45
91082	385	E	3.64	.
92682	401	E	3.32	.
110882	444	B	3.31	.
110982	445	H	10.21	6.90
51083	627	E	8.29	.
60983	657	E	6.85	.

(continued)

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TABLE A.3. (continued)

PLOT=11

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.479
11982	151	L	.	1.150
71982	332	L	.	1.150
81782	361	L	.	1.150
90982	384	B	2.59	.
91082	385	H	3.74	1.150
100482	409	E	3.23	.
101282	417	F	.	1.150
110282	434	F	.	1.150
111782	453	B	4.92	.
111782	453	H	6.07	1.150
60983	657	E	4.57	.

PLOT=13

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.575
12082	152	L	.	0.958
30882	199	L	.	0.958
42082	252	L	.	0.958
72082	333	L	.	0.958
81282	356	L	.	0.958
90982	384	E	3.58	.
92282	397	B	3.05	.
92332	398	H	4.01	0.958
92332	398	A	4.29	.
100782	412	B	3.97	.
101282	417	H	4.92	0.958
111782	453	B	4.78	.
111782	453	H	5.74	0.958
122082	486	B	4.73	.
122082	486	H	5.69	0.958
60983	657	E	4.51	.

(continued)

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TABLE A.3. (continued)

PLOT=14

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82182	0	L	.	0.2875
12082	152	L	.	0.5750
71382	332	L	.	0.5750
81282	356	L	.	0.5750
90982	384	E	1.61	.
92282	397	B	1.00	.
92382	398	H	1.58	0.5750
100782	412	B	1.36	.
101282	417	H	1.93	0.5750
110282	438	F	.	0.5750
111782	453	B	2.12	.
111782	453	H	2.70	0.5750
51083	627	E	2.70	.
60983	657	E	2.12	.

PLOT=15

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.958
12082	152	L	.	3.450
71382	332	L	.	3.450
91082	385	E	4.04	.
92682	401	E	4.08	.
110882	444	B	3.15	.
110982	445	H	10.05	6.900
51083	627	E	8.47	.
60983	657	E	7.88	.

(continued)

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TABLE A.3. (continued)

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---------------------------- PLOT=16 ------------------------------------

ANALYSIS      ELAPSED TIME      IDENTIFYING     OIL CONTENT     OIL APPLIED
DATE           (DAYS)           CODE              (% DWB)         (% DWB)

  82181              0                L              .             3.896
  11982            151                L              .             3.000
  91082            385                E            4.07              .
  92682            401                E            4.00              .
 111782            453                B            3.33              .
 111782            453                H            6.78            3.450
  60983            657                E            5.43              .
                                    SAS                           17:44 TU
---------------------------- PLOT=17 ------------------------------------

ANALYSIS      ELAPSED TIME      IDENTIFYING     OIL CONTENT     OIL APPLIED
DATE           (DAYS)           CODE              (% DWB)         (% DWB)

  82181              0                L              .             3.450
  11982            151                L              .             3.450
  91082            385                E            2.75              .
  92682            401                E            2.26              .
 111782            453                B            1.83              .
 111782            453                H            3.55            1.725
  60983            657                E            2.84              .
```

(continued)

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TABLE A.3. (continued)

PLOT=18

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.1900
11982	151	L	.	0.2875
30882	199	L	.	0.2875
71382	326	L	.	0.2875
81282	356	L	.	0.2875
92282	397	B	1.10	.
92382	398	H	1.39	0.2875
100782	412	B	1.04	.
101282	417	H	1.33	0.2875
110282	438	F	.	0.2875
111782	453	B	1.51	.
111782	453	H	1.79	0.2875
122082	486	B	1.45	.
122082	486	H	1.74	0.2875
60983	657	E	1.39	.

PLOT=20

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.863
10282	152	L	.	1.920
41582	247	L	.	1.920
72082	333	L	.	1.920
81282	356	L	.	1.920
90982	384	E	5.11	.
92282	397	B	4.50	.
92382	398	H	6.42	1.920
100782	412	B	5.47	.
101282	417	H	7.39	1.920
111782	453	B	6.56	.
111782	453	H	8.48	1.920
51033	627	E	7.01	.
60983	657	E	5.46	.

(continued)

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TABLE A.3. (continued)

------------------------------ PLOT=21 ------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	7.475
11982	151	L	.	7.420
91082	385	E	6.34	.
92682	401	E	5.13	.
110982	445	E	4.80	.
111782	453	B	4.62	.
111782	453	H	12.09	7.475
60983	657	E	7.12	.

------------------------------ PLOT=22 ------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	5.18
11982	151	L	.	11.50
91082	385	E	8.66	.
92682	401	E	6.54	.
111782	453	B	5.81	.
111782	453	H	11.56	5.75
60983	657	E	8.57	.

(continued)

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TABLE A.3. (continued)

------------------------------ PLOT=23 ------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	2.490
12082	152	L	.	7.475
72082	333	L	.	7.475
91082	385	E	9.72	.
92582	401	E	8.33	.
110982	445	E	8.02	.
122082	486	F	.	4.230
60983	657	E	6.40	.

------------------------------ PLOT=24 ------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.575
12082	152	L	.	1.725
71382	332	L	.	1.725
91082	385	E	2.73	.
92682	401	E	1.91	.
110882	444	B	1.74	.
110982	445	H	5.19	3.450
111782	453	E	4.62	.
51083	627	E	4.55	.
60983	657	E	4.13	.

(continued)

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TABLE A.3. (continued)

PLOT=25

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.2000
12082	152	L	.	0.2875
30882	199	L	.	0.2875
41582	247	L	.	0.2875
72082	333	L	.	0.2875
81282	356	L	.	0.2875
91082	385	E	1.50	.
92282	397	B	1.20	.
92382	398	H	1.49	0.2875
92382	398	A	1.60	.
100782	412	B	1.41	.
101282	417	H	1.69	0.2875
111782	453	E	1.55	.
51083	627	E	1.86	.
60983	657	E	1.33	.

PLOT=26

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	C	L	.	0.830
11982	151	L	.	1.246
30882	199	L	.	1.246
42282	254	L	.	1.246
71982	332	L	.	1.246
81782	361	L	.	1.246
90982	384	B	4.21	.
91082	385	H	5.45	1.246
100482	409	E	4.44	.
101282	417	F	.	1.246
111782	453	B	5.17	.
111782	453	H	6.42	1.246
122082	486	B	2.77	.
122082	486	H	4.02	1.246
60983	657	E	5.06	.

(continued)

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TABLE A.3. (continued)

---------------------------- PLOT=28 ----------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	1.725
12082	152	L	.	5.750
72082	333	L	.	5.750
91082	385	E	8.46	.
92682	401	E	6.65	.
110982	445	B	6.55	.
110982	445	H	18.05	11.500
60983	657	E	11.32	.

---------------------------- PLOT=29 ----------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	1.725
12082	152	L	.	3.520
72082	333	L	.	5.750
91082	385	E	5.79	.
92682	401	E	5.49	.
110982	445	B	4.88	.
110982	445	H	16.48	11.500
51083	627	E	9.81	.
60983	657	E	9.98	.

(continued)

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TABLE A.3. (continued)

PLOT=30

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	5.75
12082	152	L	.	6.90
91082	385	E	4.50	.
92682	401	E	3.15	.
110832	444	E	2.85	.
111782	453	E	2.74	.
122032	486	B	1.94	.
122082	486	H	5.39	3.45
41183	598	E	5.20	.
51083	627	E	4.79	.
60983	657	E	2.51	.

PLOT=31

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	3.450
11982	151	L	.	3.450
91082	385	E	2.00	.
92682	401	E	1.91	.
111782	453	B	1.66	.
111782	453	H	3.39	1.725
60983	657	E	1.87	.

(continued)

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TABLE A.3. (continued)

PLOT=32

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
32181	0	L	.	0.319
11982	151	L	.	0.575
30882	199	L	.	0.575
42082	252	L	.	0.575
81782	361	L	.	0.575
90982	384	E	2.17	.
92282	397	B	2.01	.
92382	398	H	2.58	0.575
92382	398	A	2.77	.
100482	409	E	2.54	.
100782	412	E	2.18	.
101482	419	J	2.27	.
101482	419	A	2.84	0.575
111782	453	B	2.43	.
111782	453	H	3.01	0.575
122082	486	B	1.84	.
122082	486	H	2.15	0.575
60983	657	E	2.27	.

(continued)

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TABLE A.3. (continued)

PLOT=34

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82131	0	L	.	0.575
11982	151	L	.	0.958
30882	199	L	.	0.958
41532	237	L	.	0.958
71382	326	L	.	0.958
81232	356	L	.	0.958
90962	384	E	3.10	.
92232	397	B	2.79	.
92382	398	H	3.74	0.958
101432	419	J	3.77	.
101482	419	A	4.72	0.958
122082	436	B	2.99	.
122082	486	H	3.95	0.958
51083	627	E	4.22	.
60983	657	E	4.19	.

PLOT=35

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	5.175
12032	152	L	.	6.807
91032	385	E	5.37	.
92682	401	E	4.14	.
110832	444	E	3.87	.
111782	453	E	3.66	.
122032	436	B	2.48	.
122032	486	H	8.23	5.750
41183	593	E	7.82	.
51083	627	E	6.40	.
60983	657	E	5.24	.

(continued)

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TABLE A.3. (continued)

---------------------------- PLOT=36 ------------------------------------

ANALYSIS DATE	ELAPSED TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	2.492
11982	151	L	.	6.090
71982	332	L	.	4.040
91082	385	E	8.42	.
122082	486	B	4.53	.
122082	486	H	8.51	3.973
60983	657	E	7.32	.

---------------------------- PLOT=38 ------------------------------------

ANALYSIS DATE	ELAPSEC TIME (DAYS)	IDENTIFYING CODE	OIL CONTENT (% DWB)	OIL APPLIED (% DWB)
82181	0	L	.	0.575
12082	152	L	.	1.725
71382	326	L	.	1.725
91082	385	E	3.50	.
110982	445	B	2.65	.
110982	445	H	6.10	3.450
60983	657	E	4.11	.

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TABLE A.4. RAW FRACTIONATION DATA - PLOTS 30 and 35

Plot	Elapsed Day	% Oil In Soil	% Asph. In Oil	% Sat. In Oil	% Arom. In Oil	% Polar In Oil
30	385	4.39	4.68	48.46	30.74	19.12
	385	4.91	4.10	43.27	30.74	16.85
	385	4.19	4.88	48.30	30.74	24.34
	401	3.18	5.81	40.45	28.20	25.43
	401	3.14	6.11	40.32	28.20	24.83
	401	3.13	5.79	41.50	28.20	25.12
	444	2.90	8.85	30.63	27.33	33.20
	444	2.75	8.64	29.94	26.85	34.57
	444	2.90	8.32	36.49	12.29	42.90
	486	1.91	3.90	23.84	36.72	35.54
	486	2.02	3.20	15.70	55.03	26.07
	486	1.88	5.71	19.45	33.70	41.15
	598	4.26	5.34	33.40	24.66	36.59
	598	5.60	5.66	30.59	27.20	36.55
	598	9.47	5.15	30.92	27.27	36.66
	627	5.40	5.85	.	.	.
	627	5.15	6.03	.	.	.
	627	4.75	7.56	.	.	.
	657	2.57	4.00	42.61	13.66	39.72
	657	4.51	5.43	35.33	28.15	31.09
	657	2.49	4.61	31.46	31.19	.
35	385	5.13	6.94	48.51	20.59	23.97
	385	5.36	5.70	35.11	12.52	44.67
	385	5.63	4.48	19.28	35.95	40.29
	401	4.15	.	44.21	.	36.21
	401	4.33	.	43.22	.	37.49
	401	4.63	.	43.22	.	37.49
	444	3.84	8.26	30.69	24.97	36.08
	444	3.82	8.32	24.67	30.32	38.69
	444	3.95	9.76	28.83	23.77	37.64
	486	2.56	4.37	20.27	36.72	38.15
	486	2.54	6.18	20.34	35.32	4.92
	486	2.33	4.89	22.90	35.05	19.07
	598	8.42	7.75	33.16	21.27	37.82
	598	6.07	5.65	41.72	19.68	32.95
	598	8.98	6.69	36.40	19.69	21.10
	627	6.97	6.49	.	.	.
	627	6.35	6.84	.	.	.
	627	6.23	7.43	.	.	.
	657	5.11	4.90	38.07	31.43	25.59
	657	3.42	5.36	44.62	11.40	38.29
	657	5.38	5.87	12.68	31.43	25.59

TABLE A.5--LEGEND FOR FIGURES A.1 to A.32

A -- 'After' application sample
B -- 'Before' application sample
E -- 'Extra' sample not associated with application
F -- 'Failed' to sample on application date
H -- 'Hypothetical After' sample
J -- 'Hypothetical Before' sample
L -- 'Loading' only, no sample

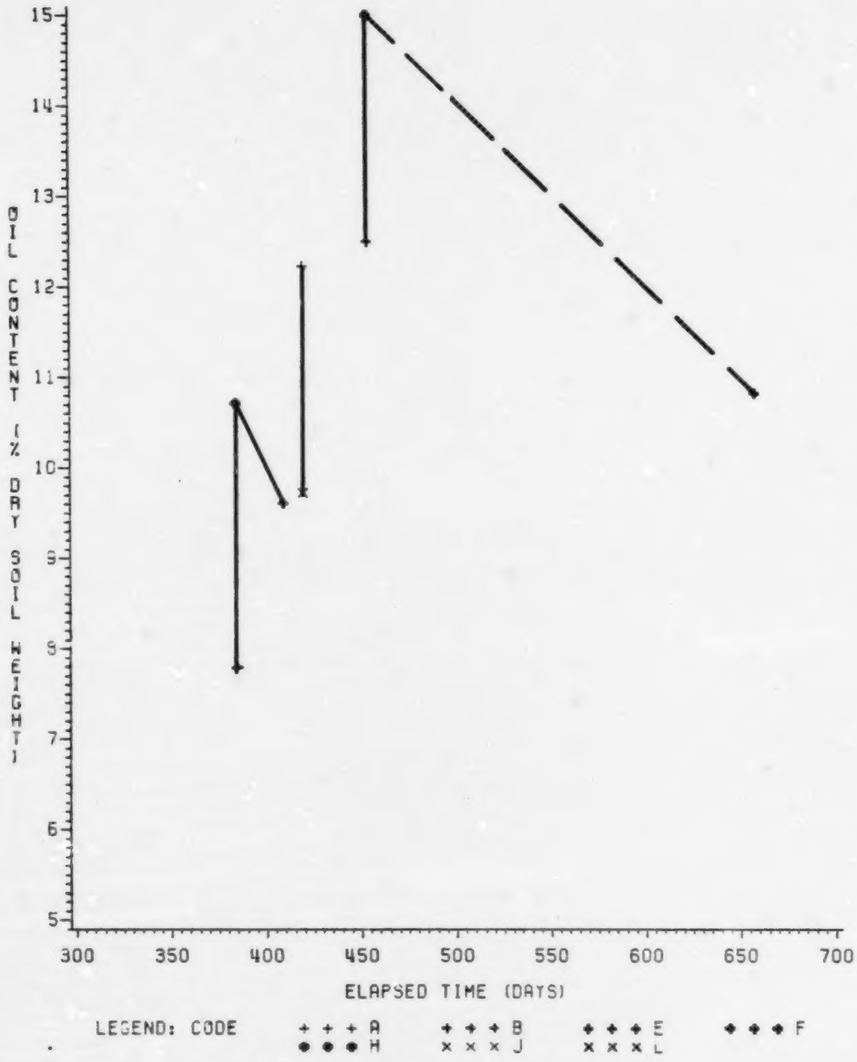

Figure A.1. Time series oil content history, plot 1.

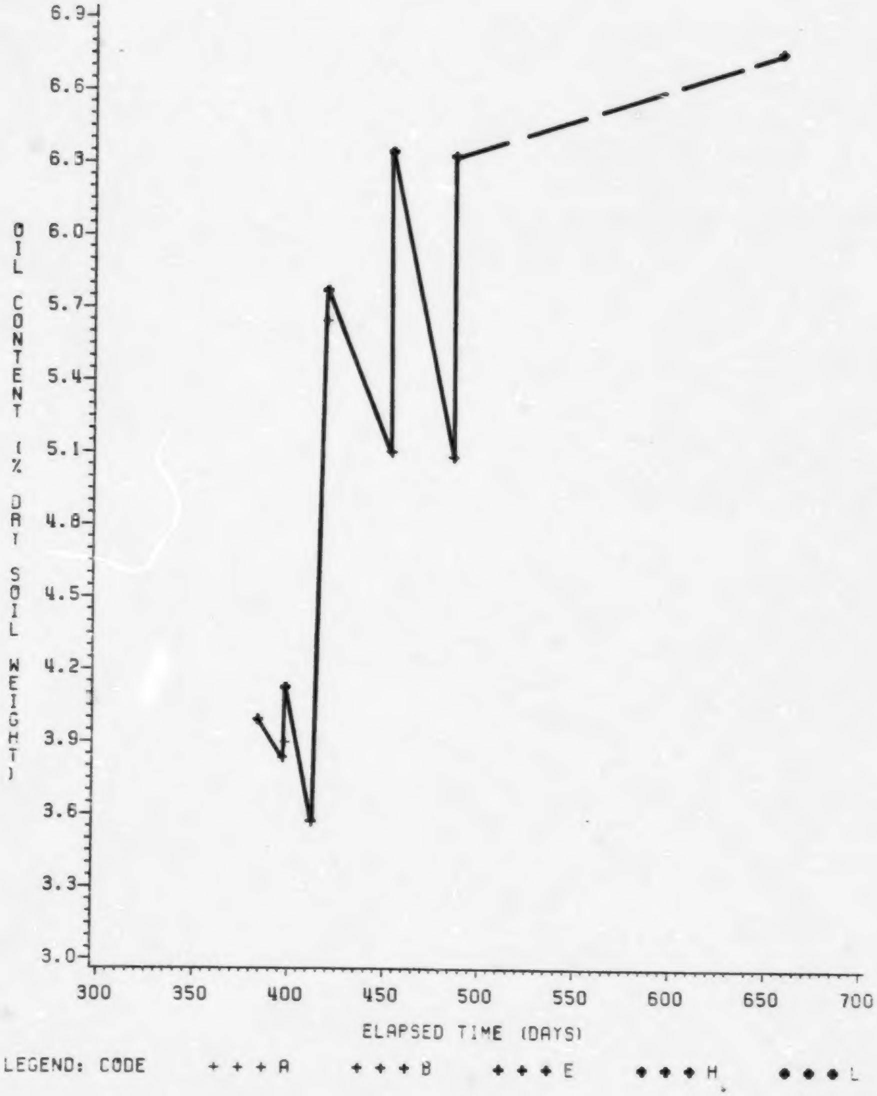

Figure A.2. Time series oil content history, plot 2.

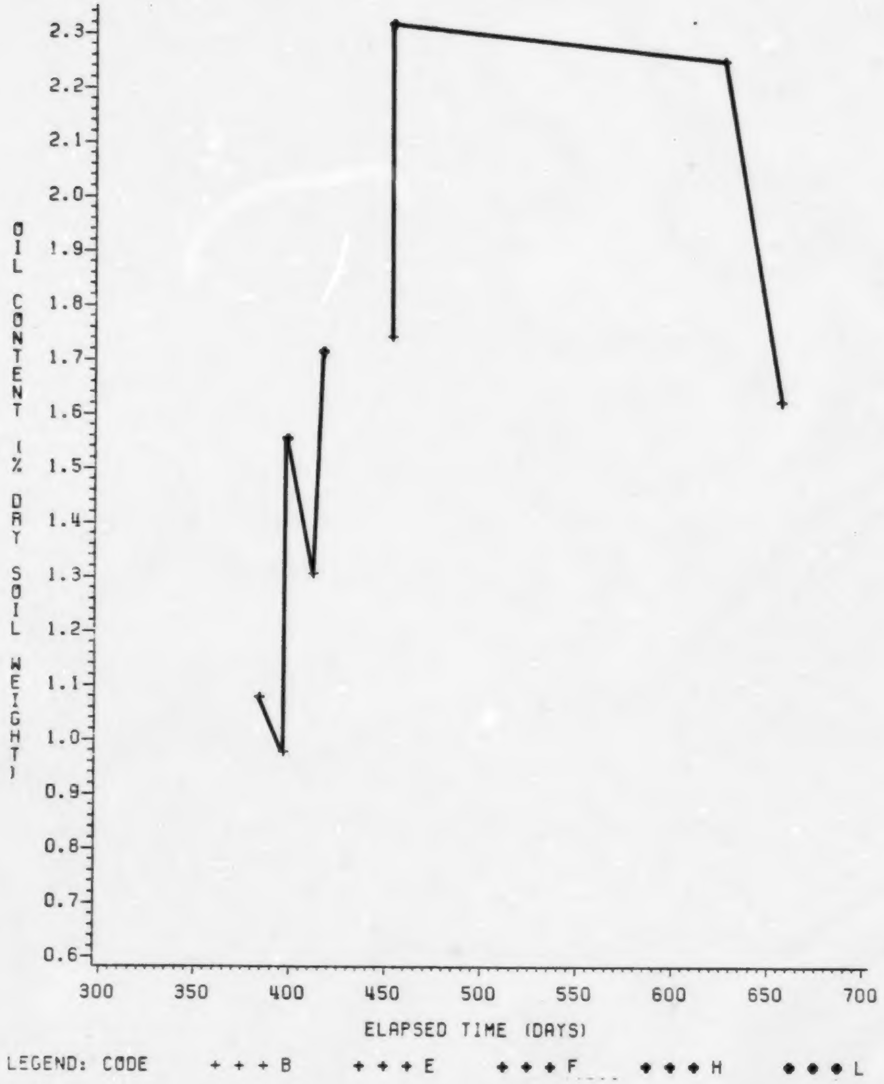

Figure A.3. Time series oil content history, plot 4.

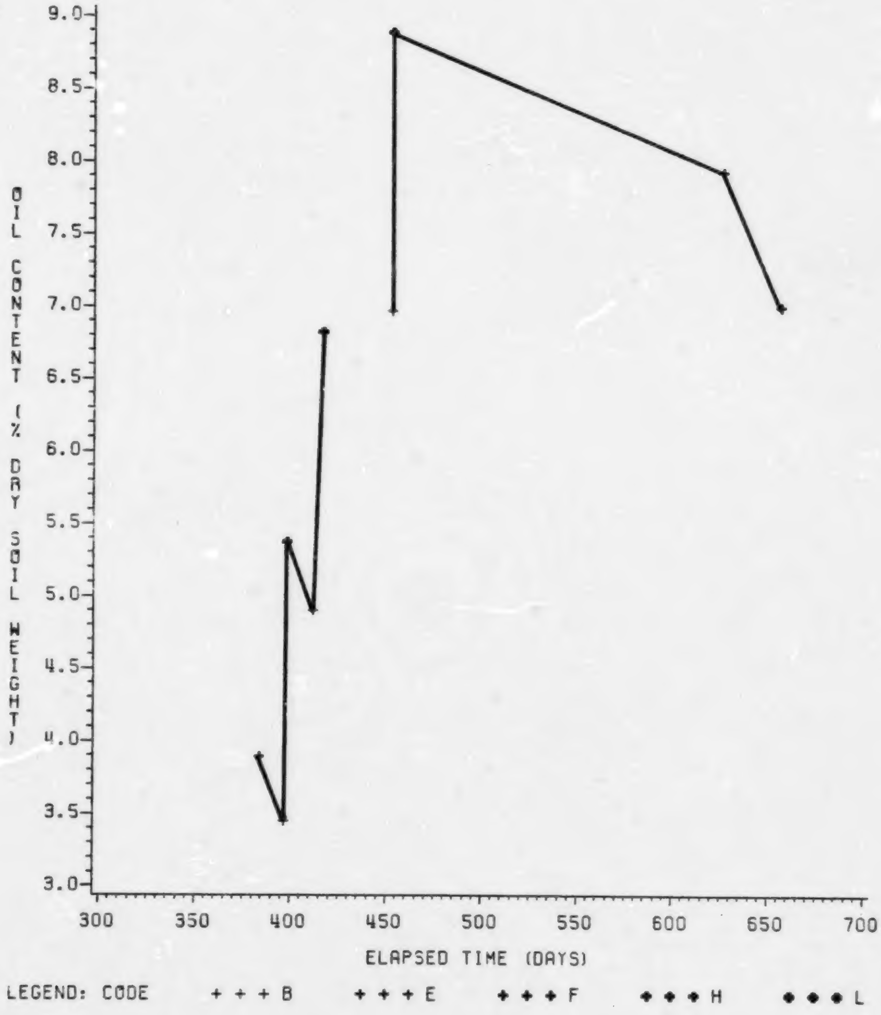

Figure A.4. Time series oil content history, plot 5.

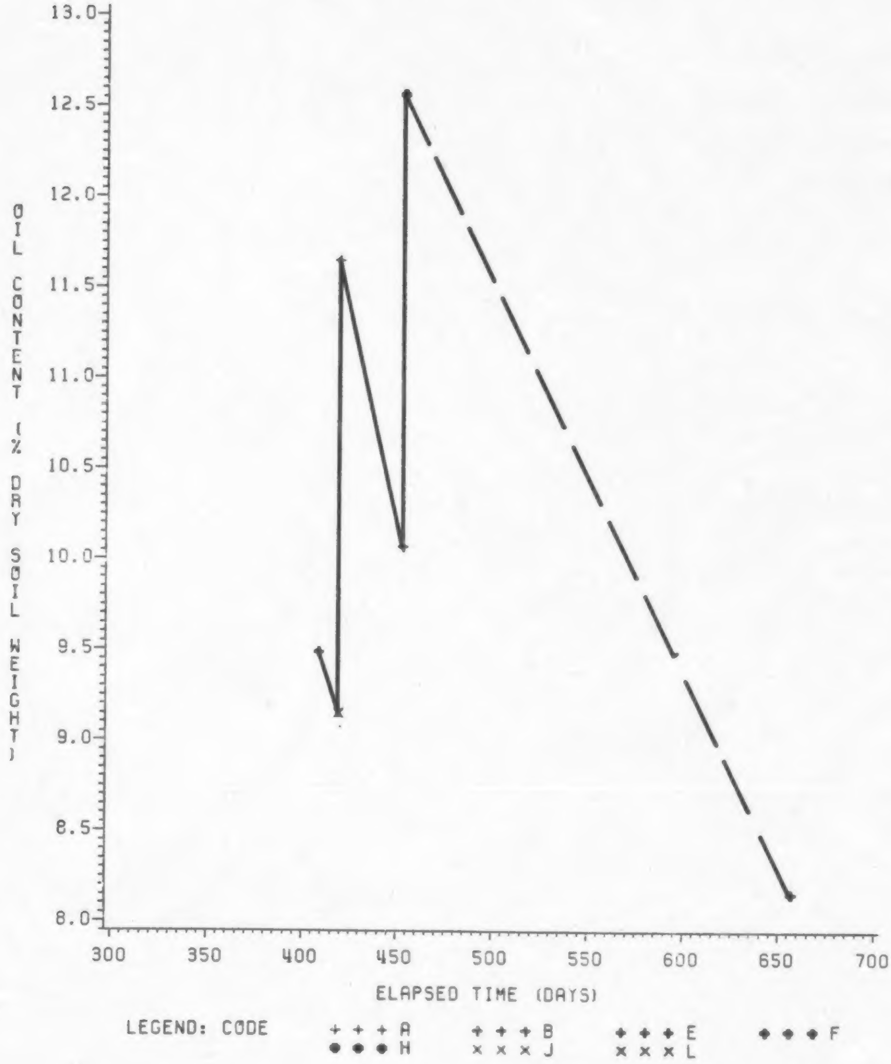

Figure A.5. Time series oil content history, plot 6.

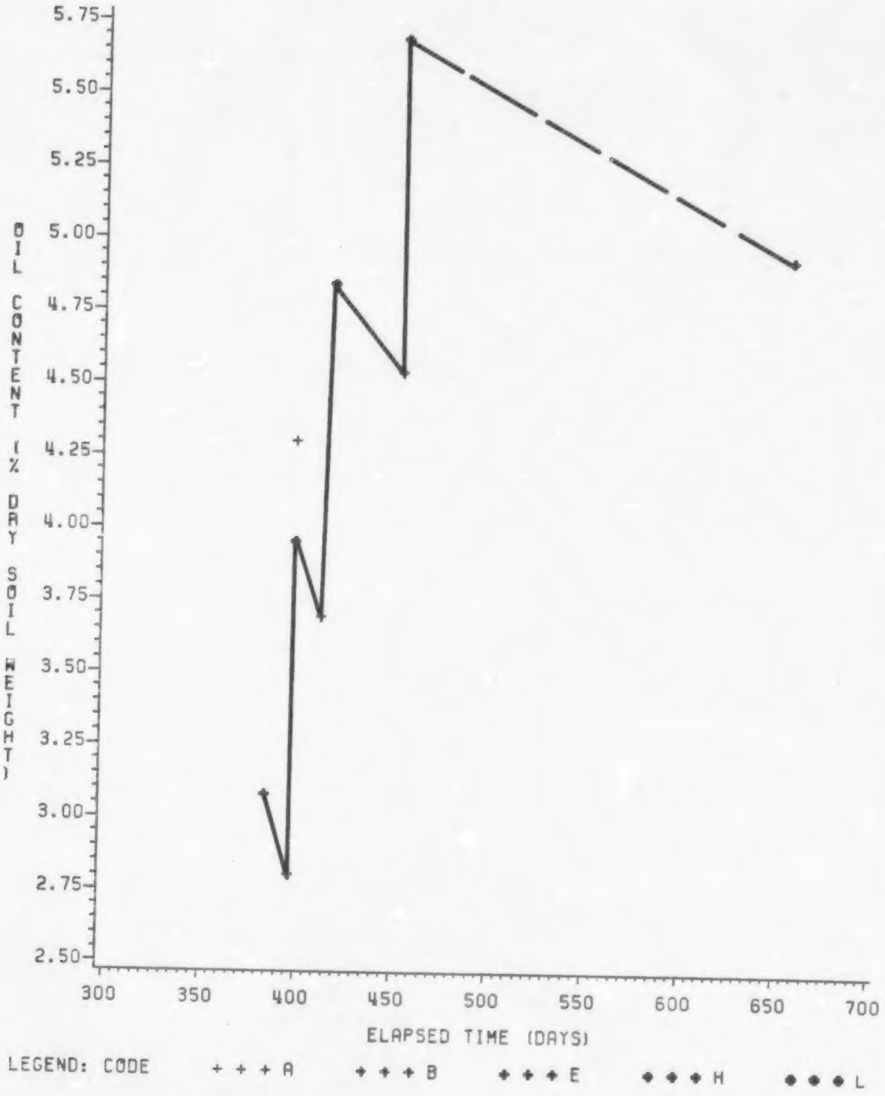

Figure A.6. Time series oil content history, plot 7.

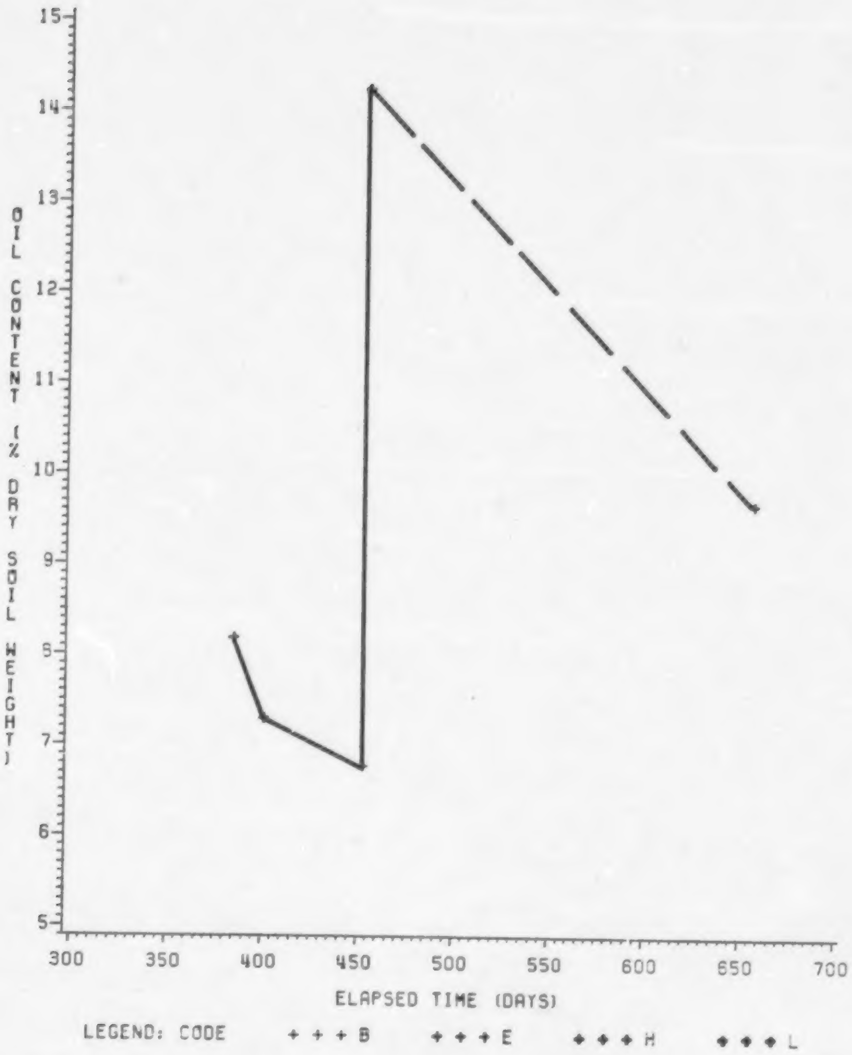

Figure A.7. Time series oil content history, plot 8.

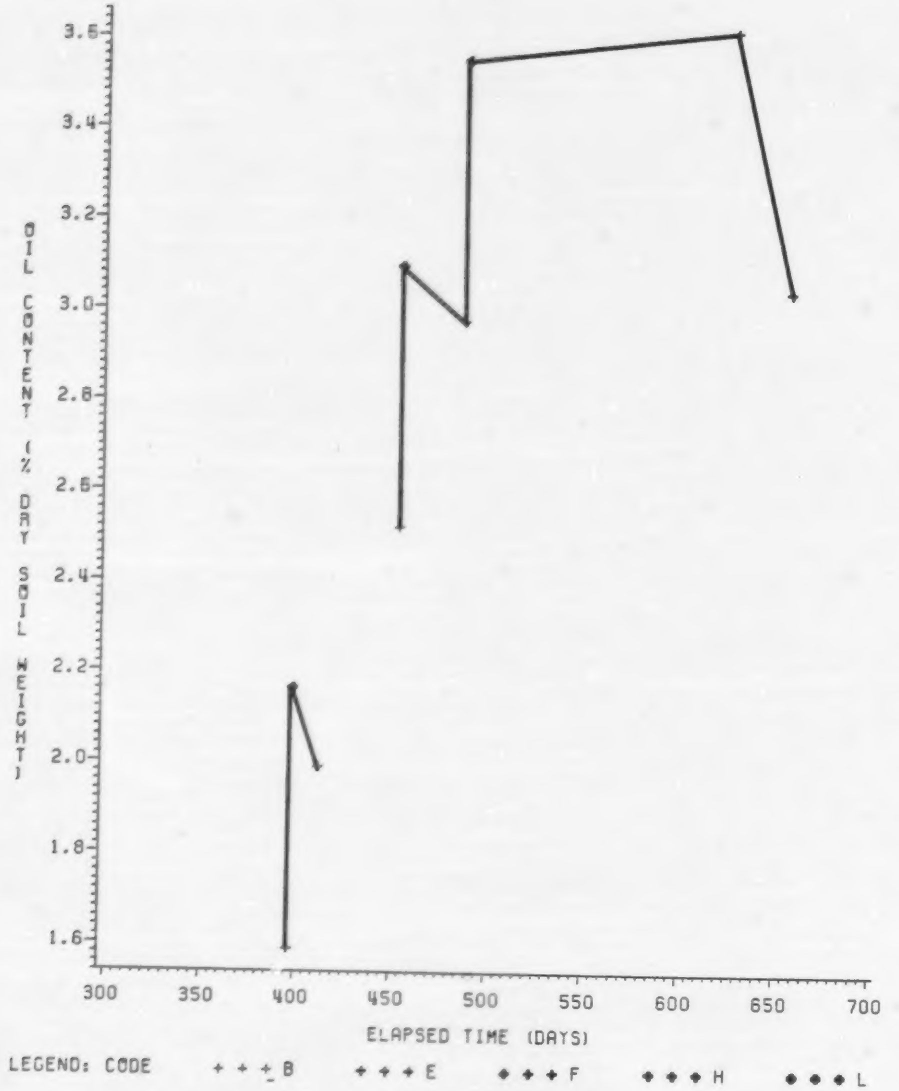

Figure A.8. Time series oil content history, plot 9.

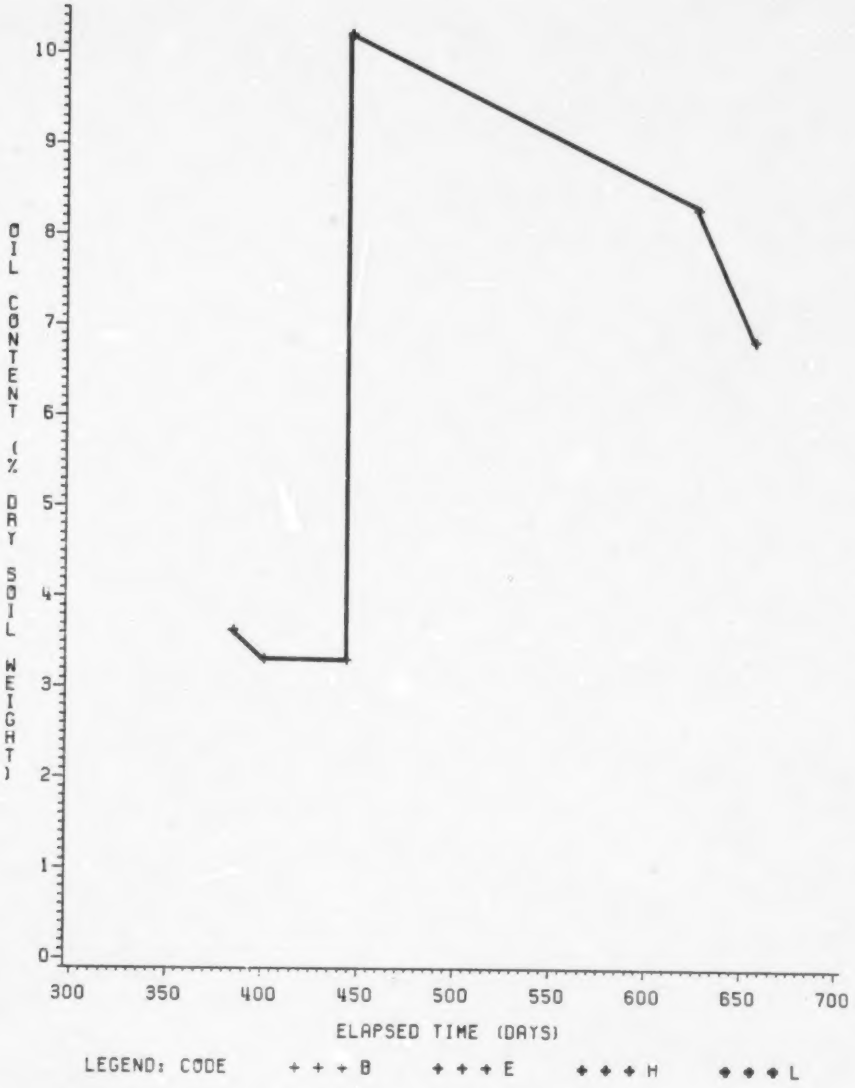

Figure A.9. Time series oil content history, plot 10.

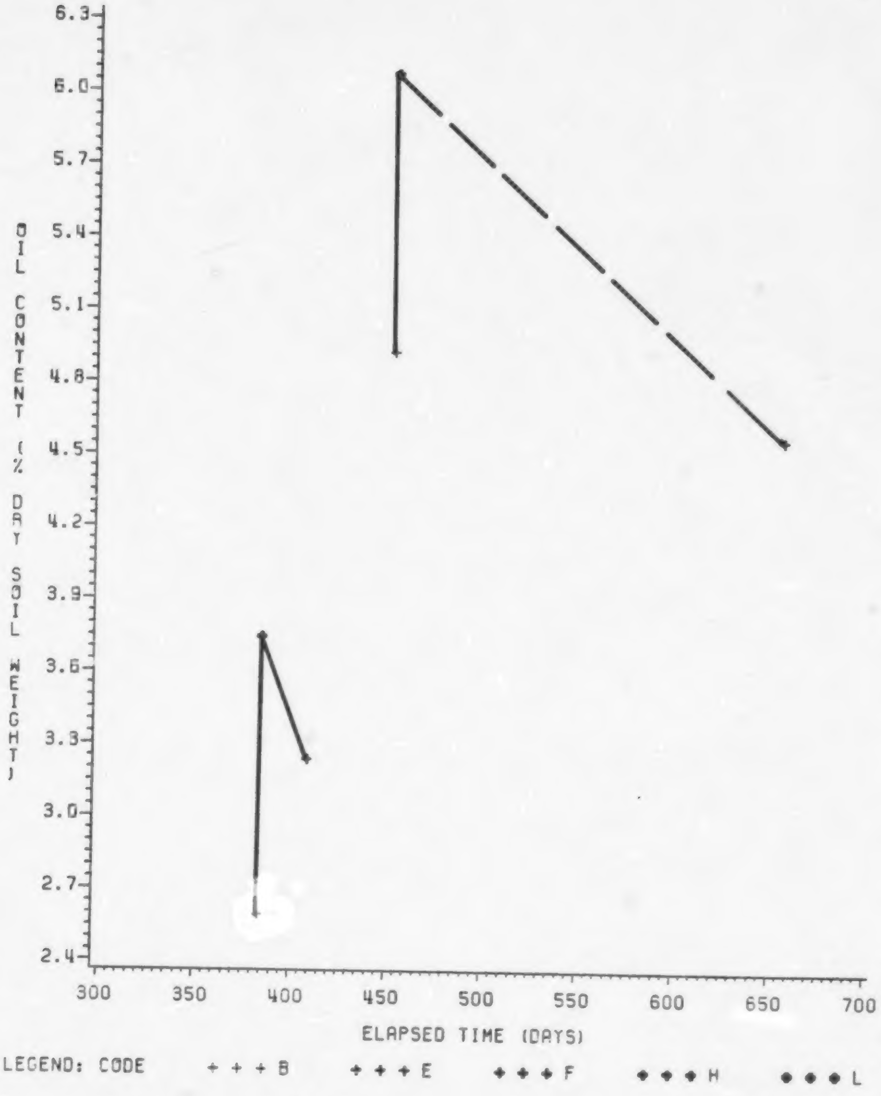

Figure A.10. Time series oil content history, plot 11.

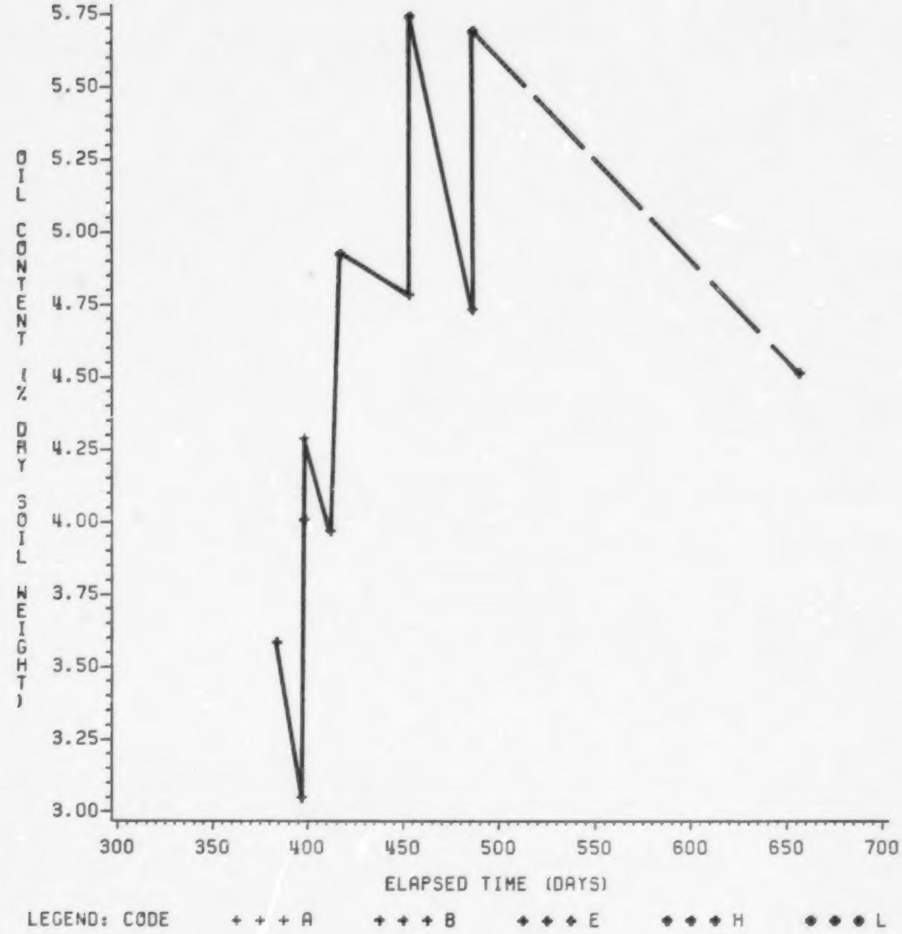

Figure A.11. Time series oil content history, plot 13.

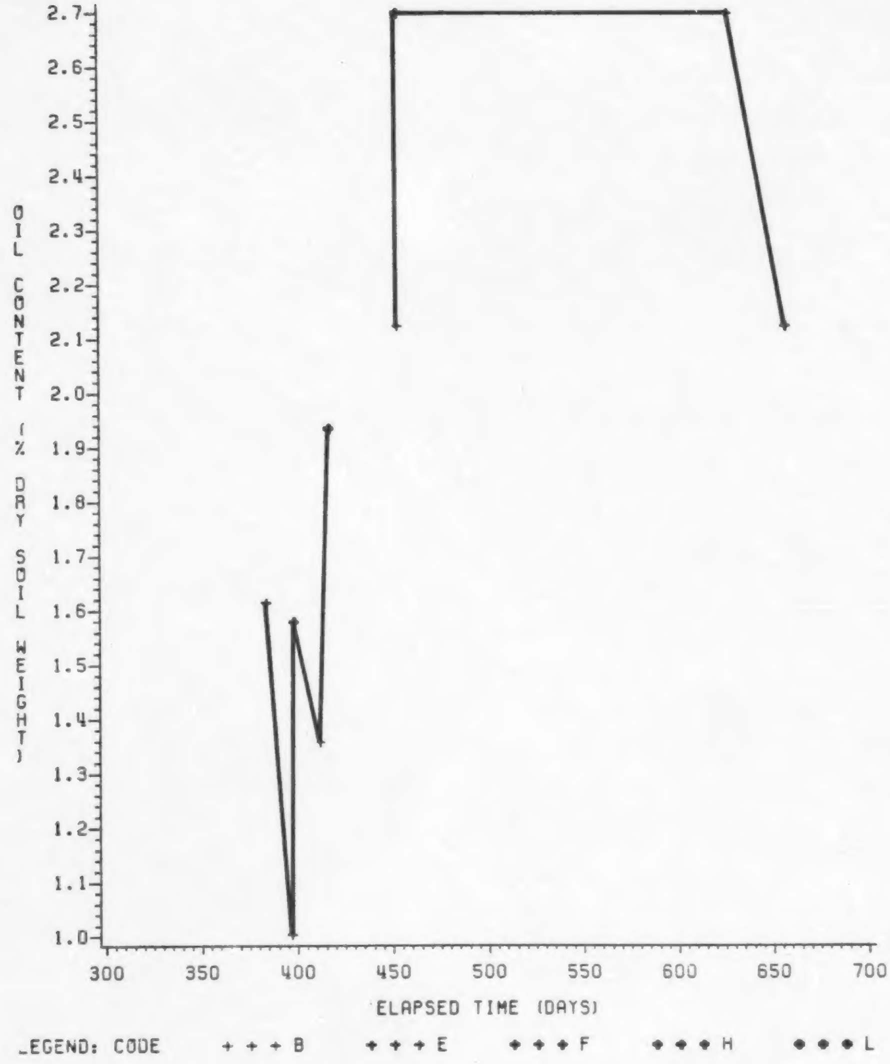

Figure A.12. Time series oil content history, plot 14.

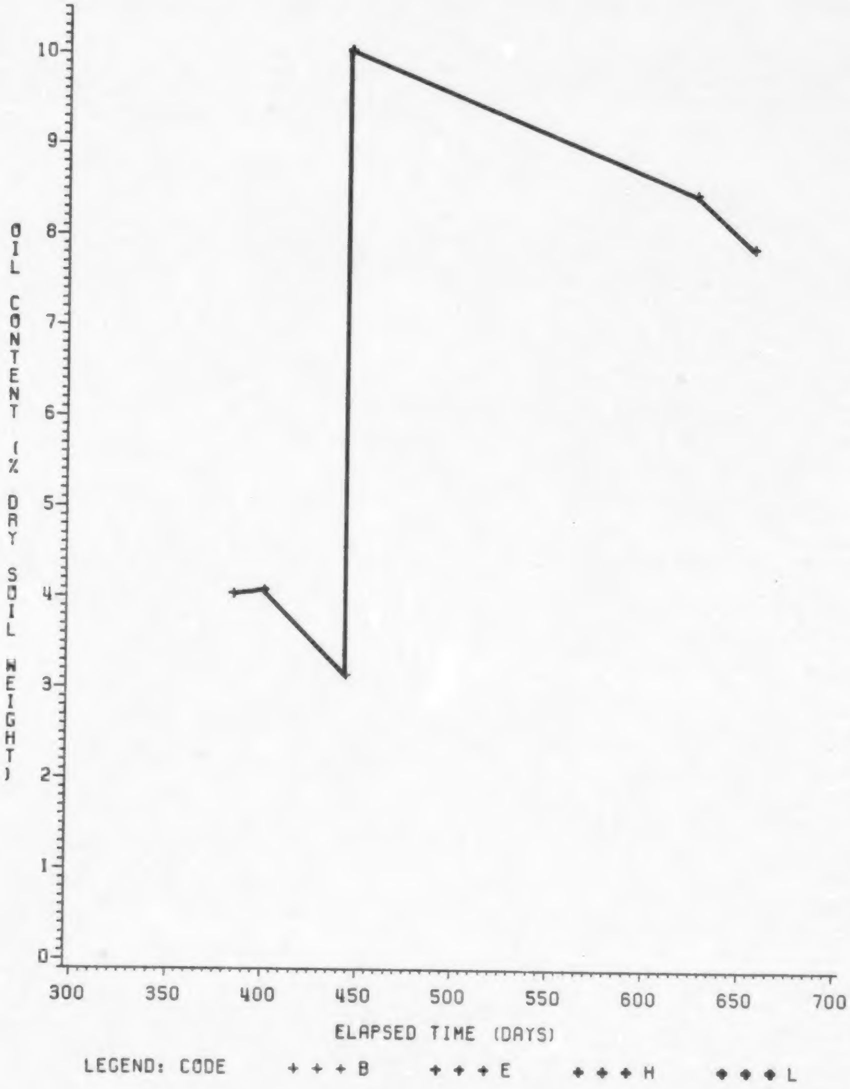

Figure A.13. Time series oil content history, plot 15.

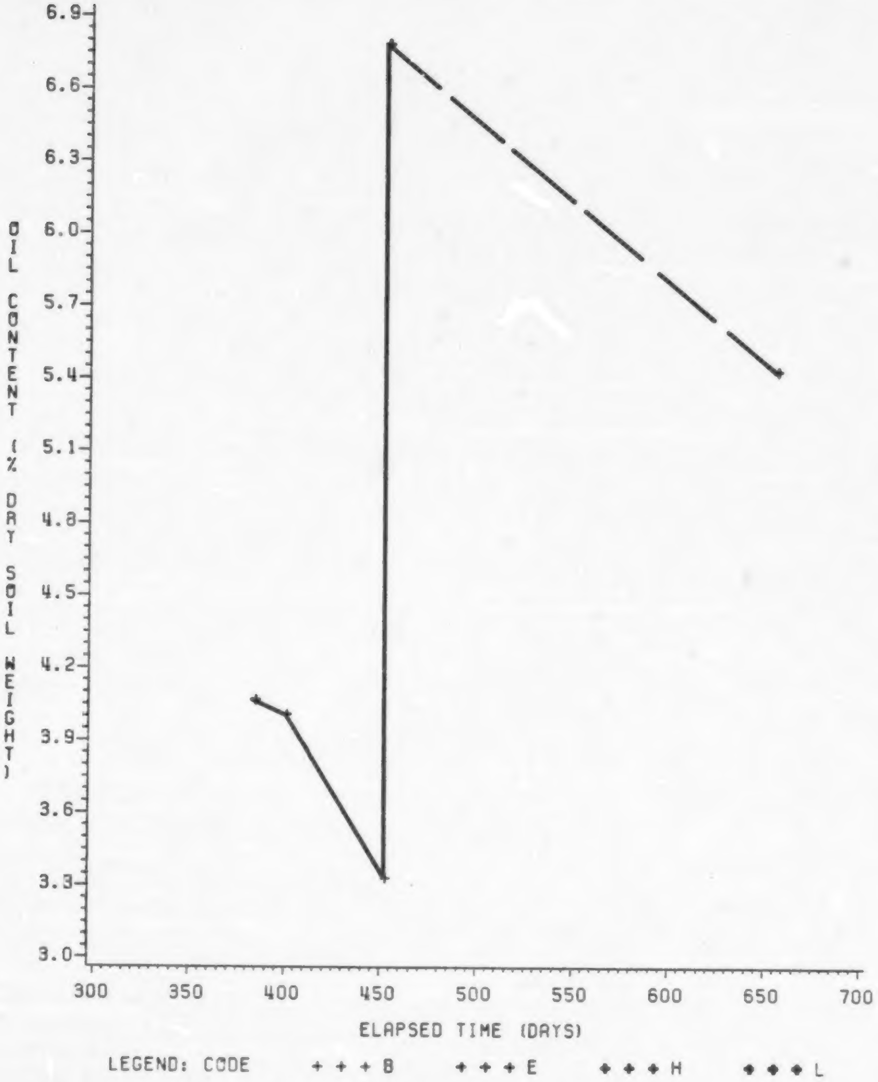

Figure A.14. Time series oil content history, plot 16.

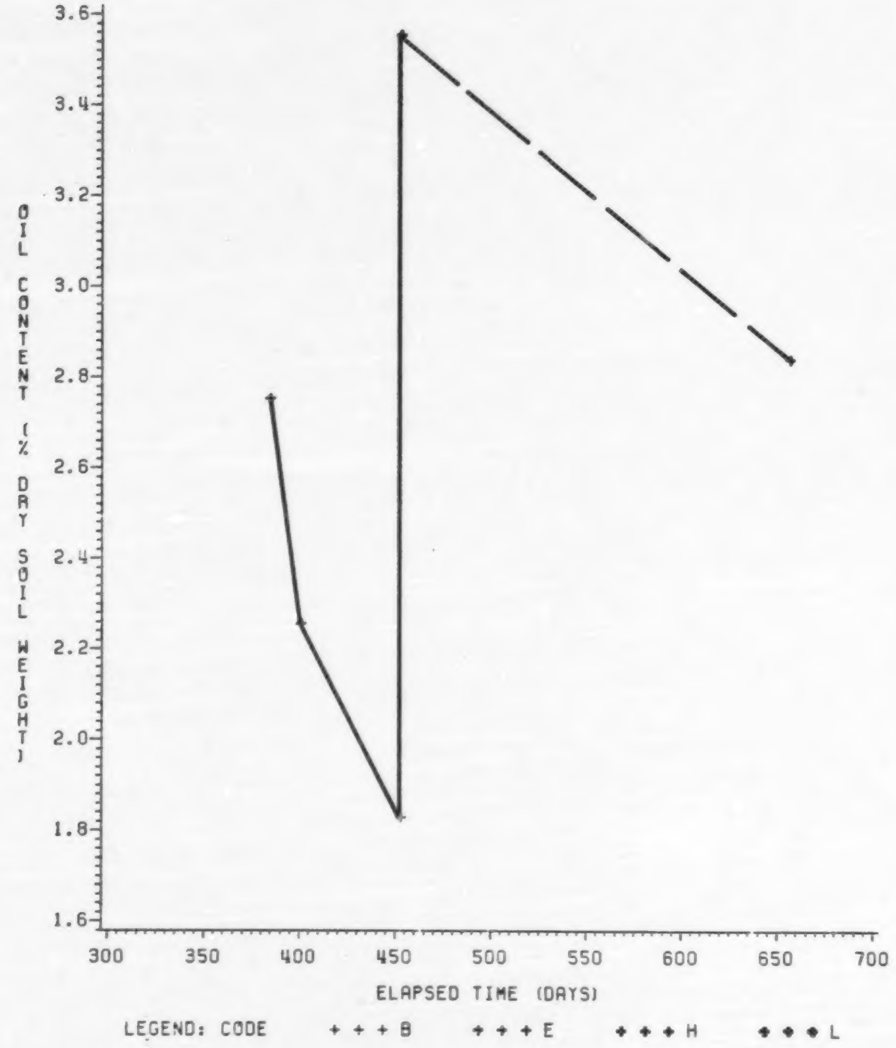

Figure A.15. Time series oil content history, plot 17.

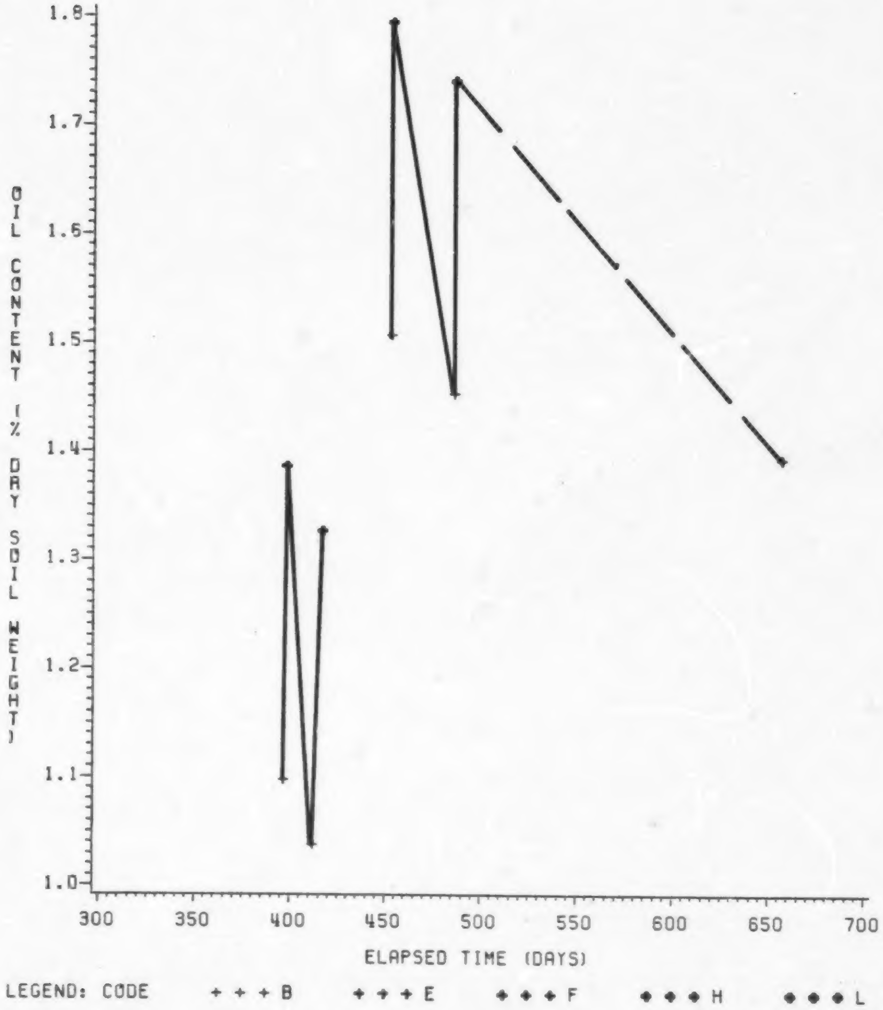

Figure A.16. Time series oil content history, plot 18.

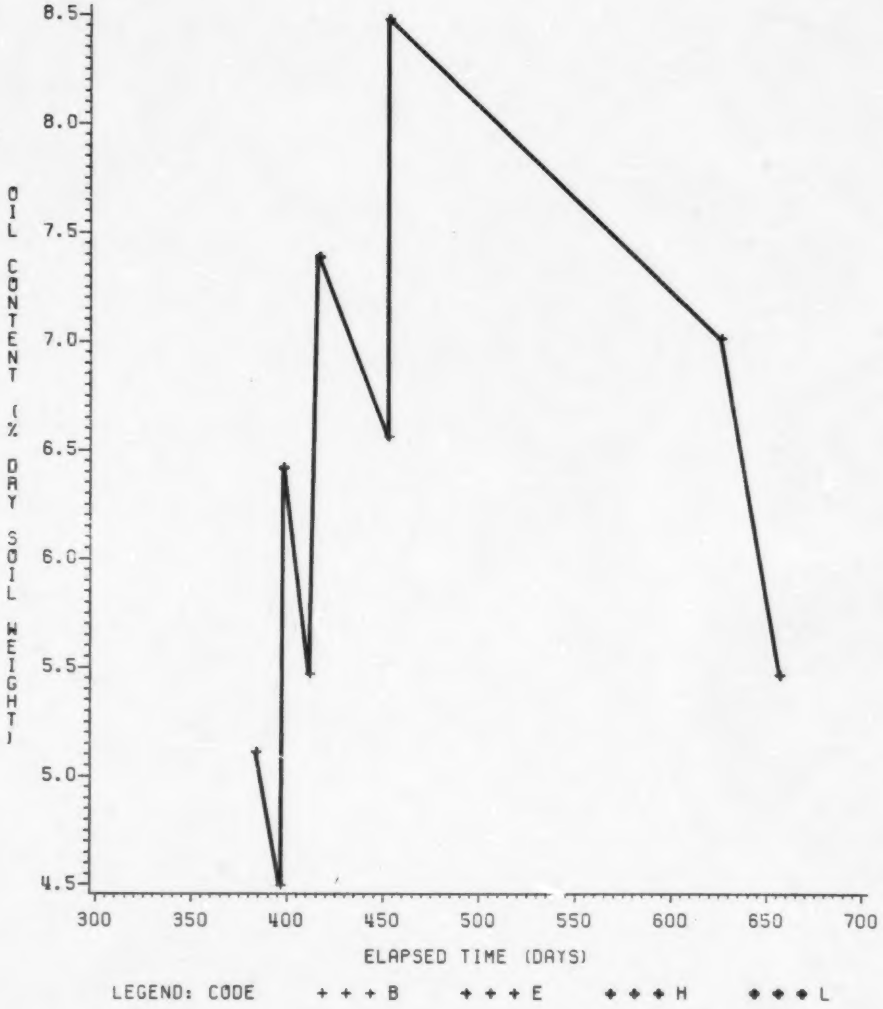

Figure A.17. Time series oil content history, plot 20.

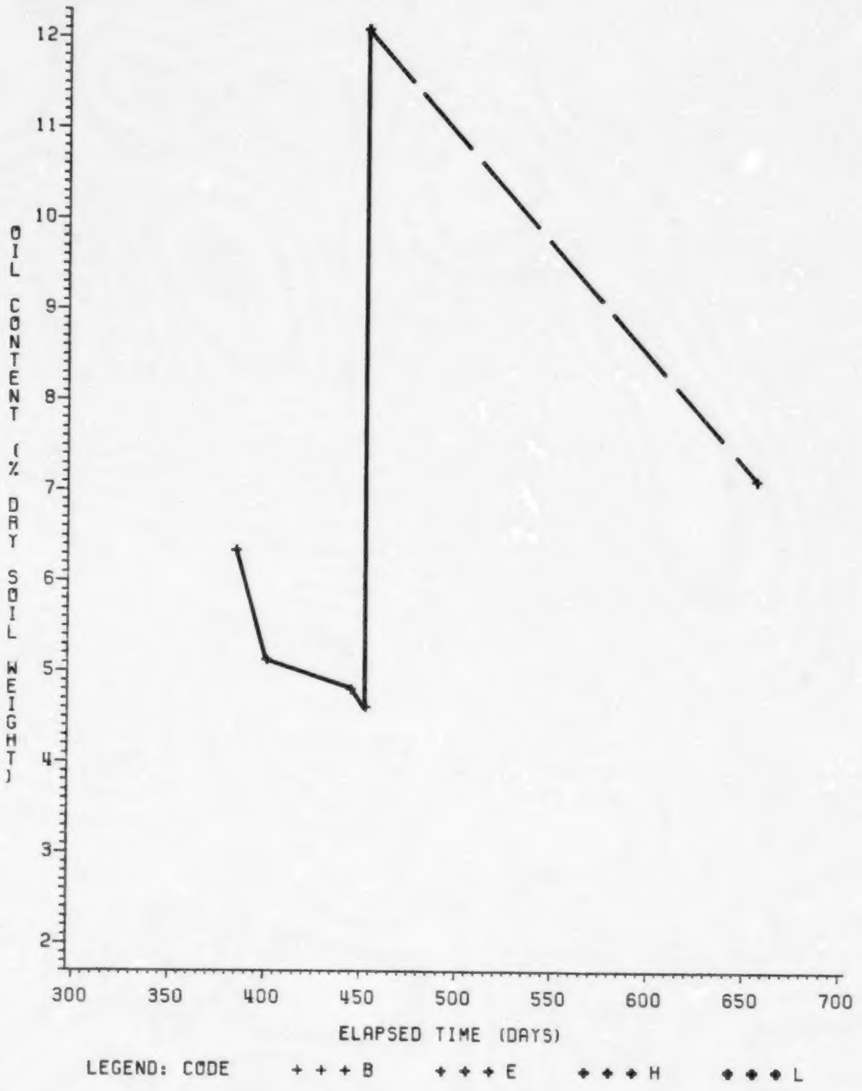

Figure A.18. Time series oil content history, plot 21.

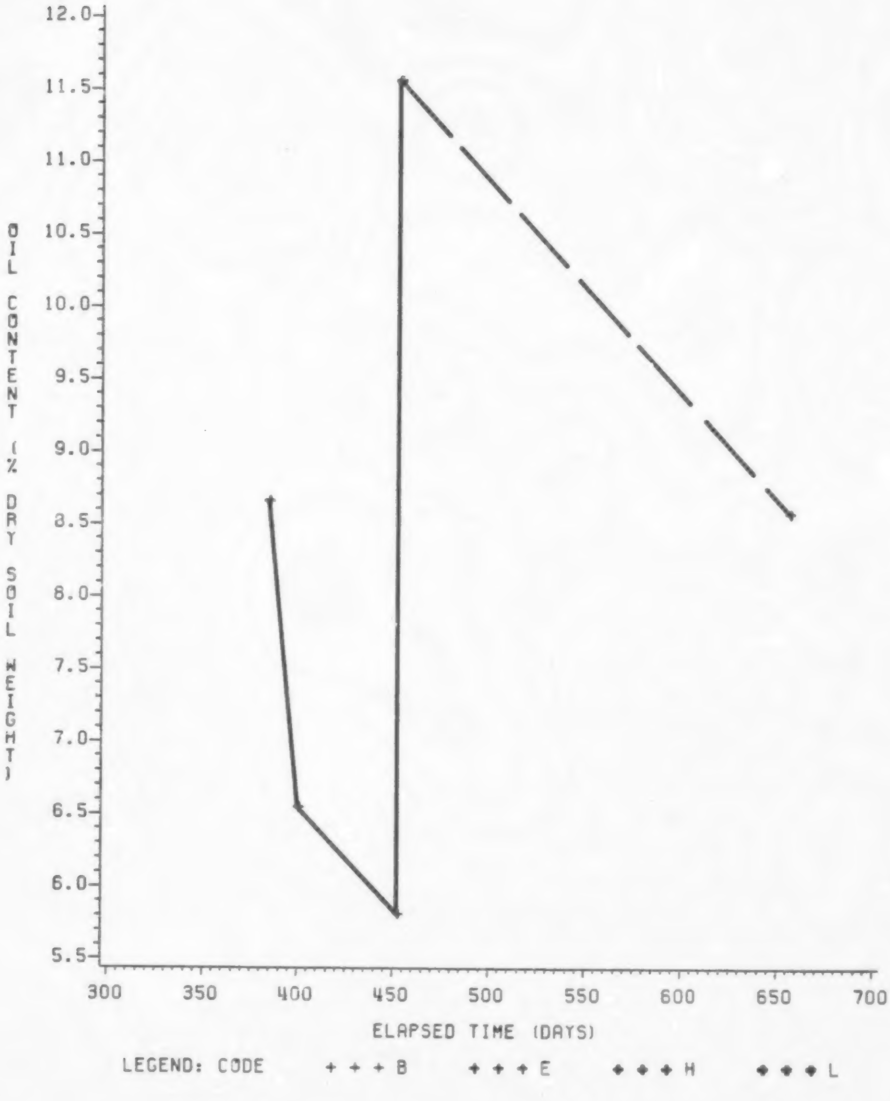

Figure A.19. Time series oil content history, plot 22.

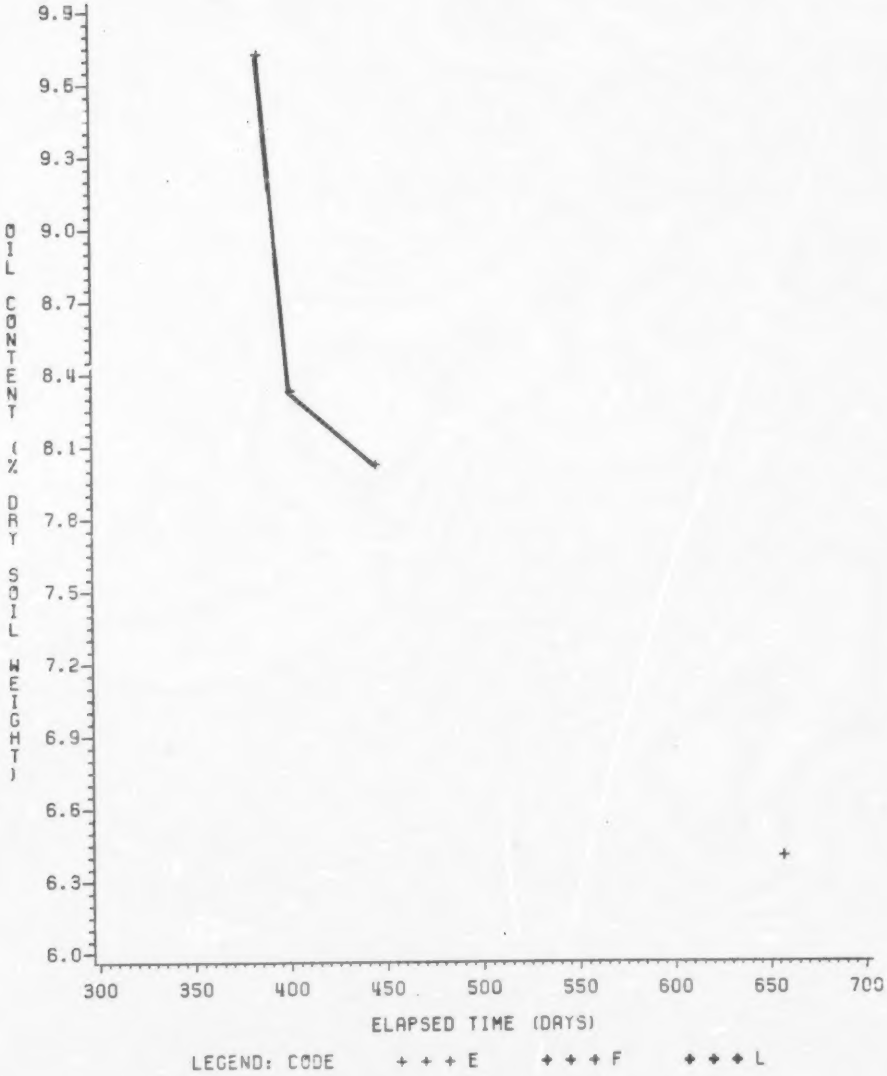

Figure A.20. Time series oil content history, plot 23.

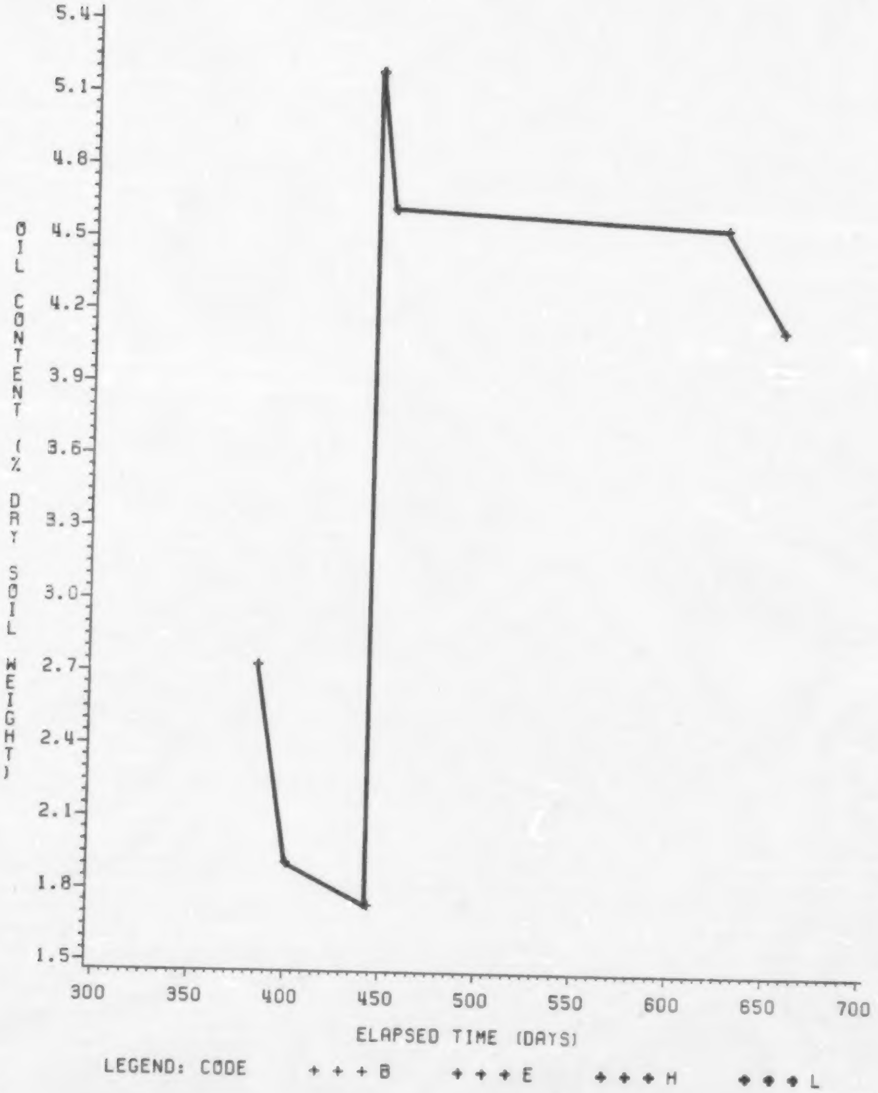

Figure A.21. Time series oil content history, plot 24.

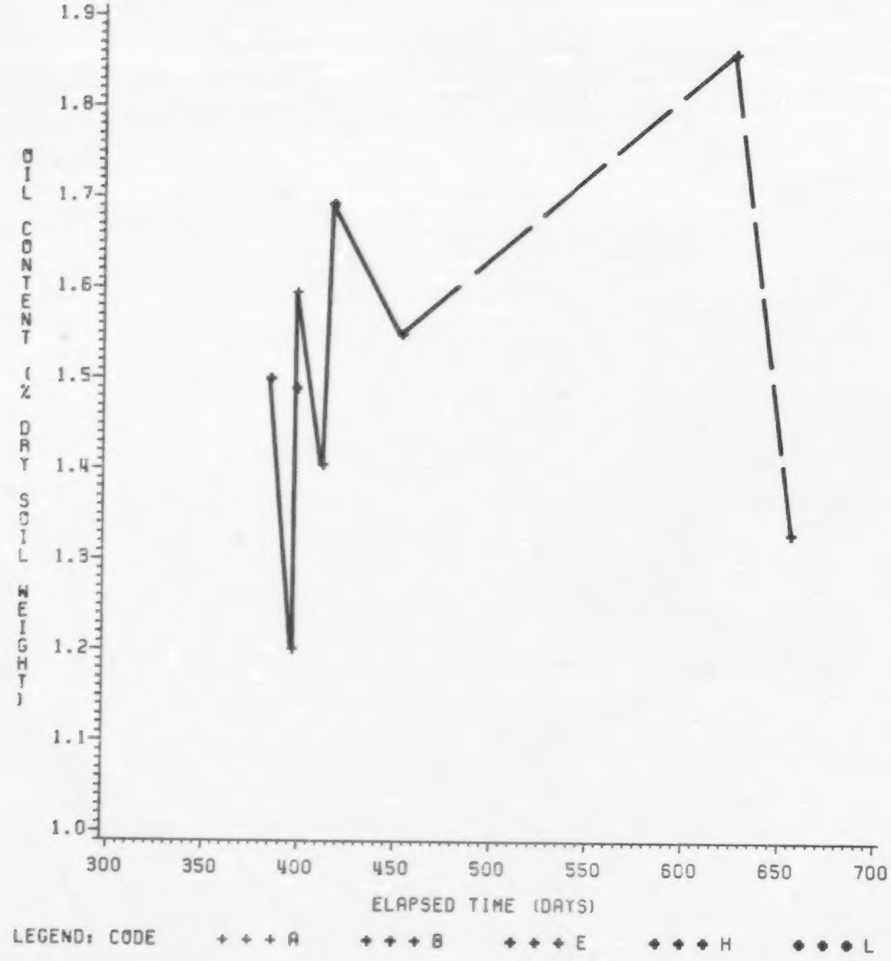

Figure A.22. Time series oil content history, plot 25.

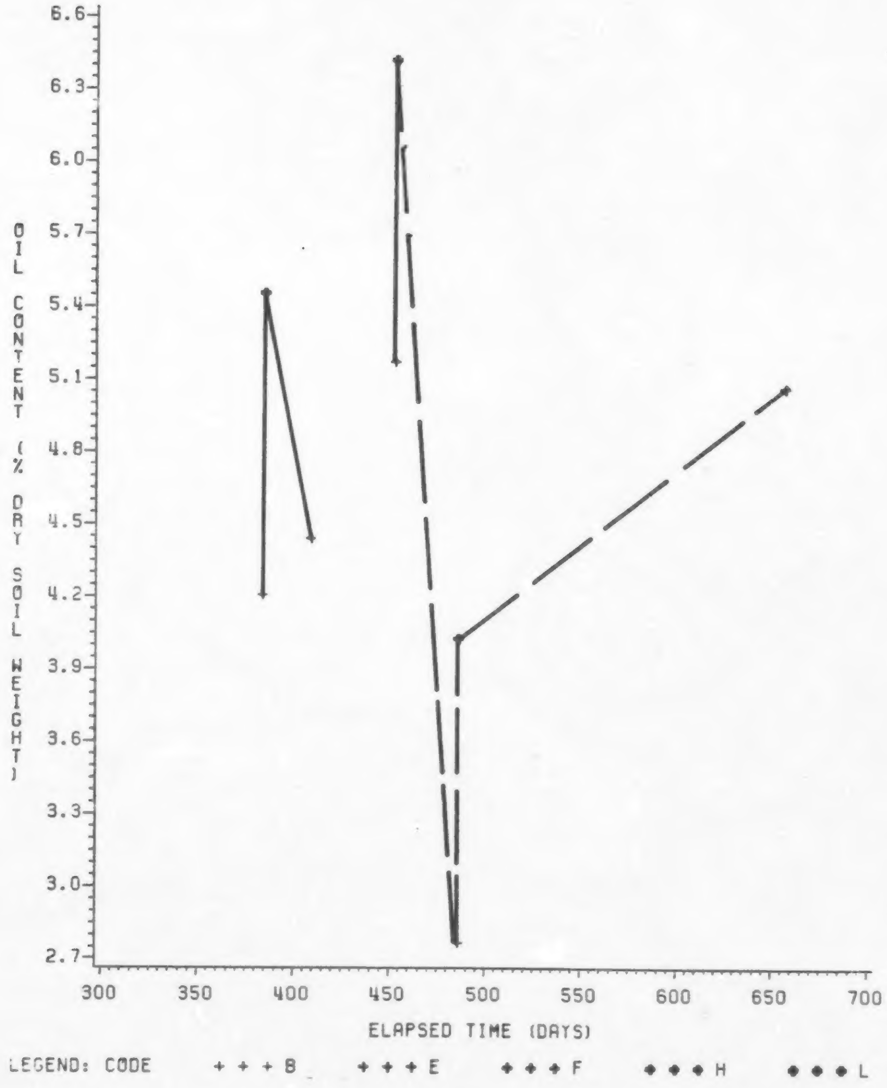

Figure A.23. Time series oil content history, plot 26.

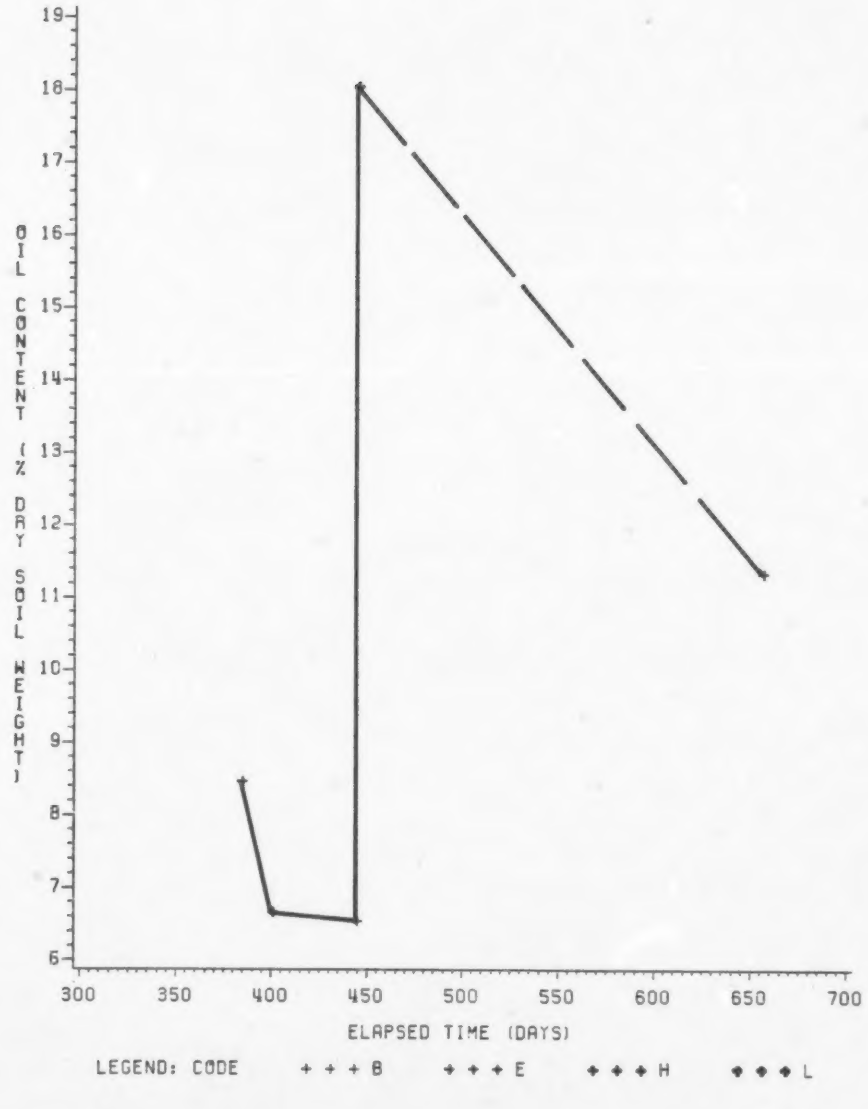

Figure A.24. Time series oil content history, plot 28.

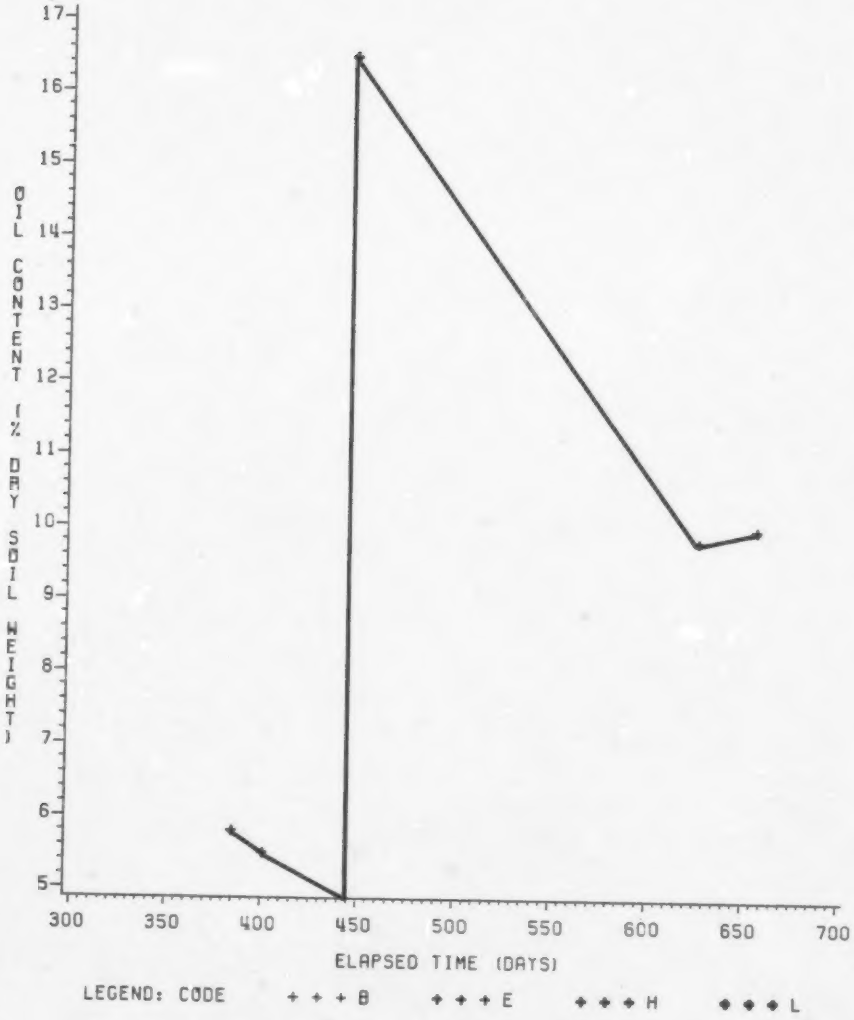

Figure A.25. Time series oil content history, plot 29.

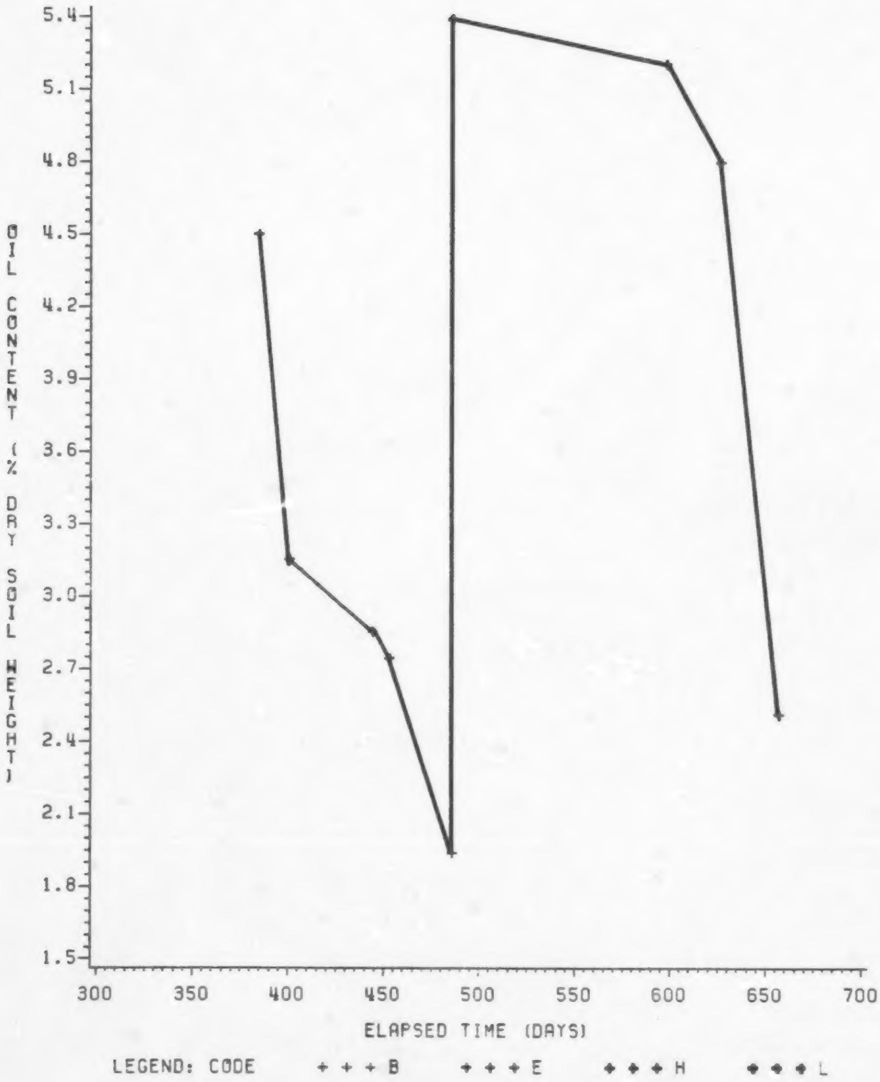

Figure A.26. Time series oil content history, plot 30.

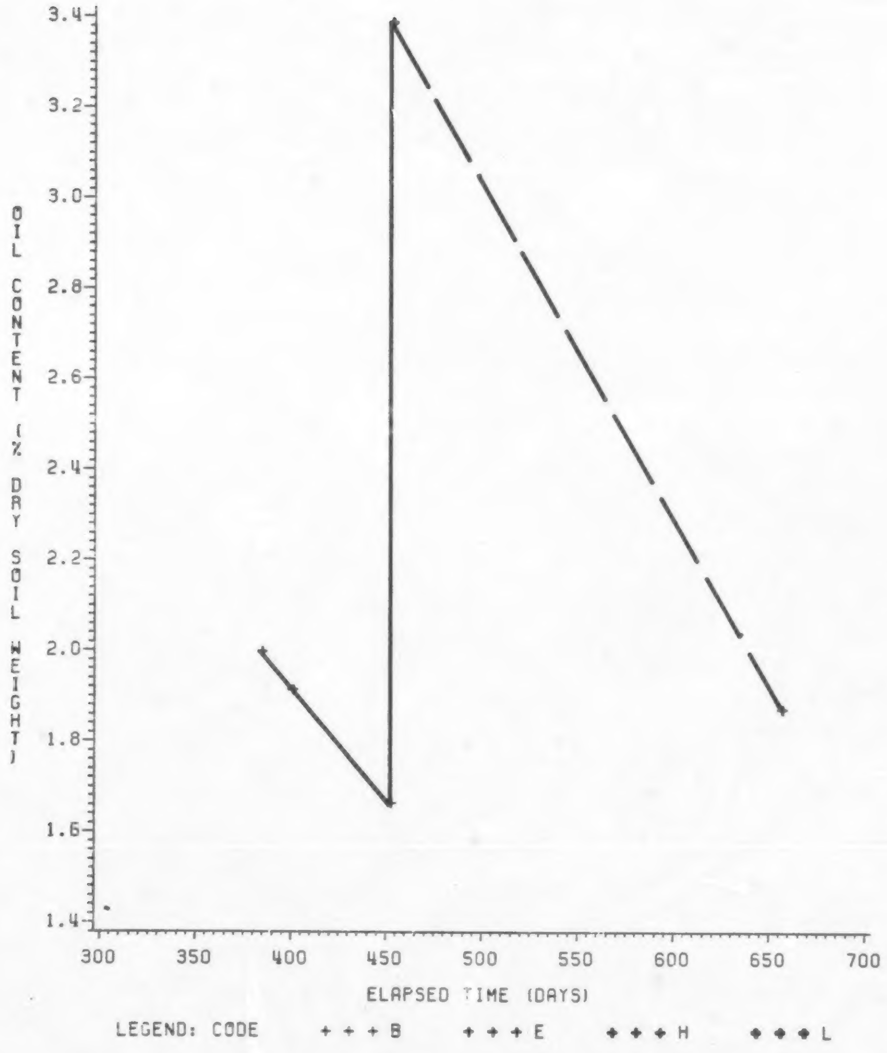

Figure A.27. Time series oil content history, plot 31.

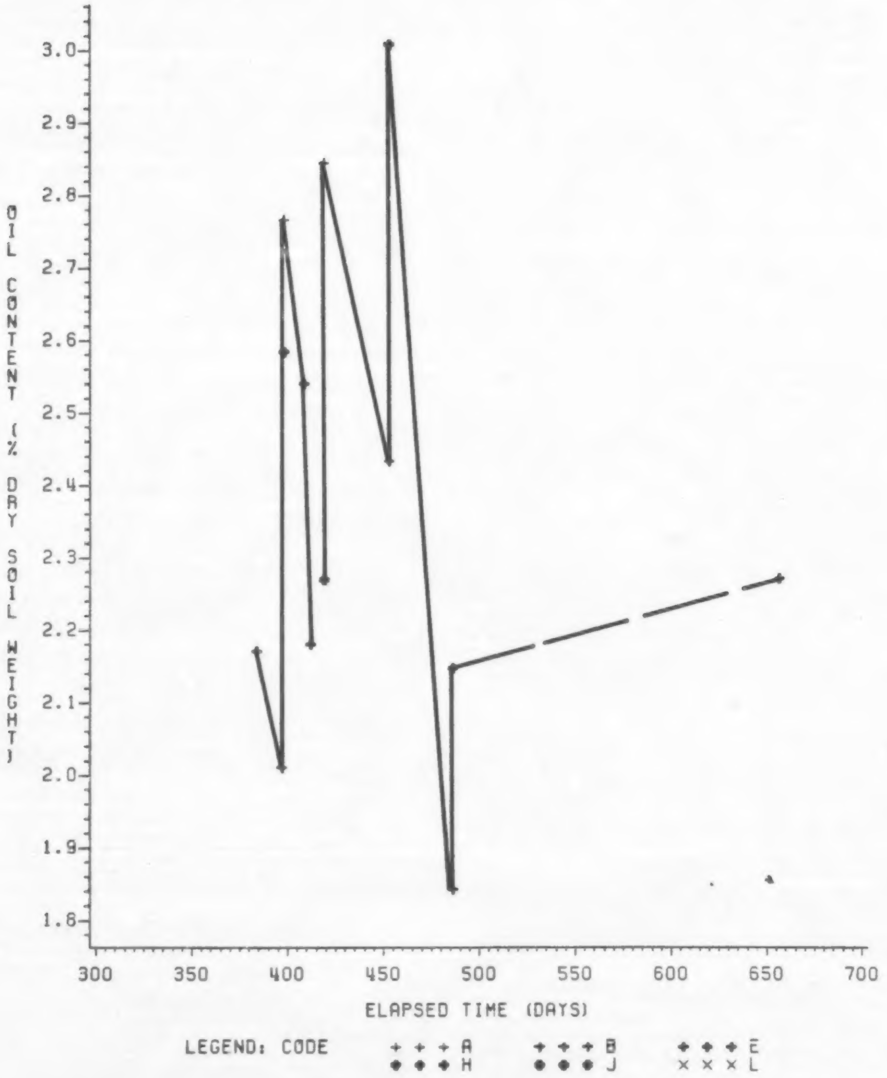

Figure A.28. Time series oil content history, plot 32.

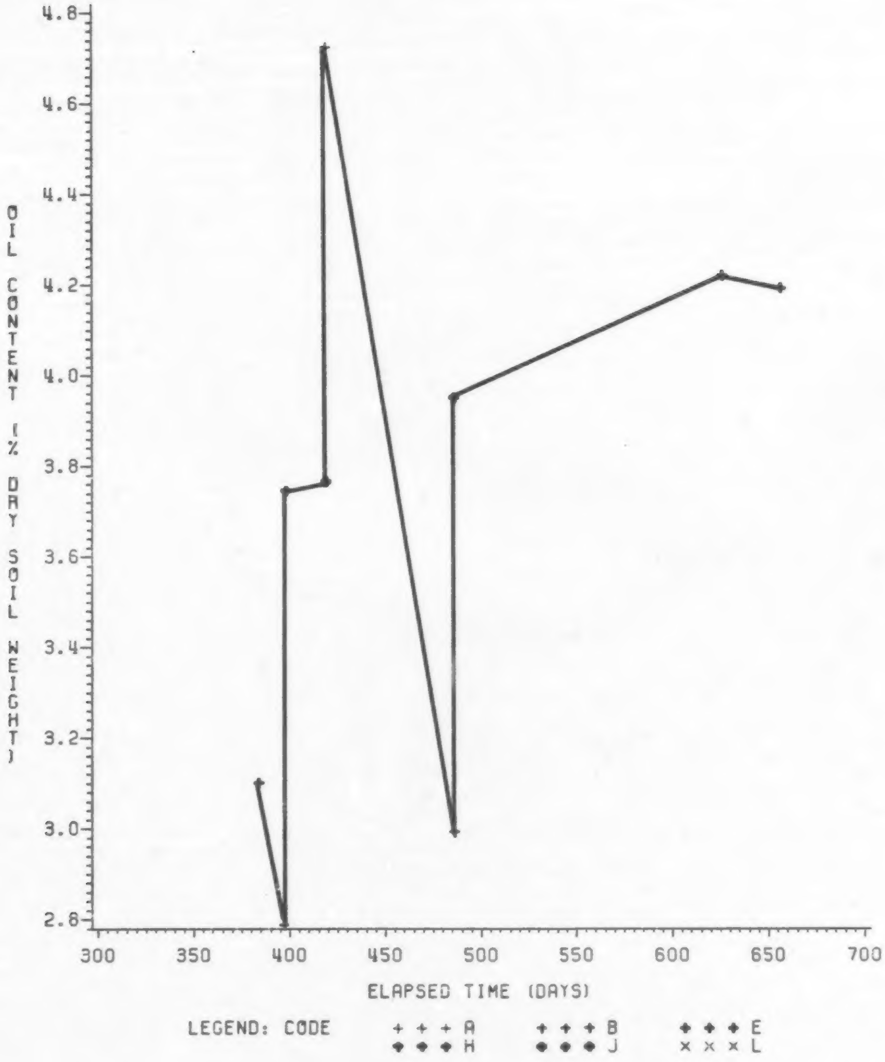

Figure A.29. Time series oil content history, plot 34.

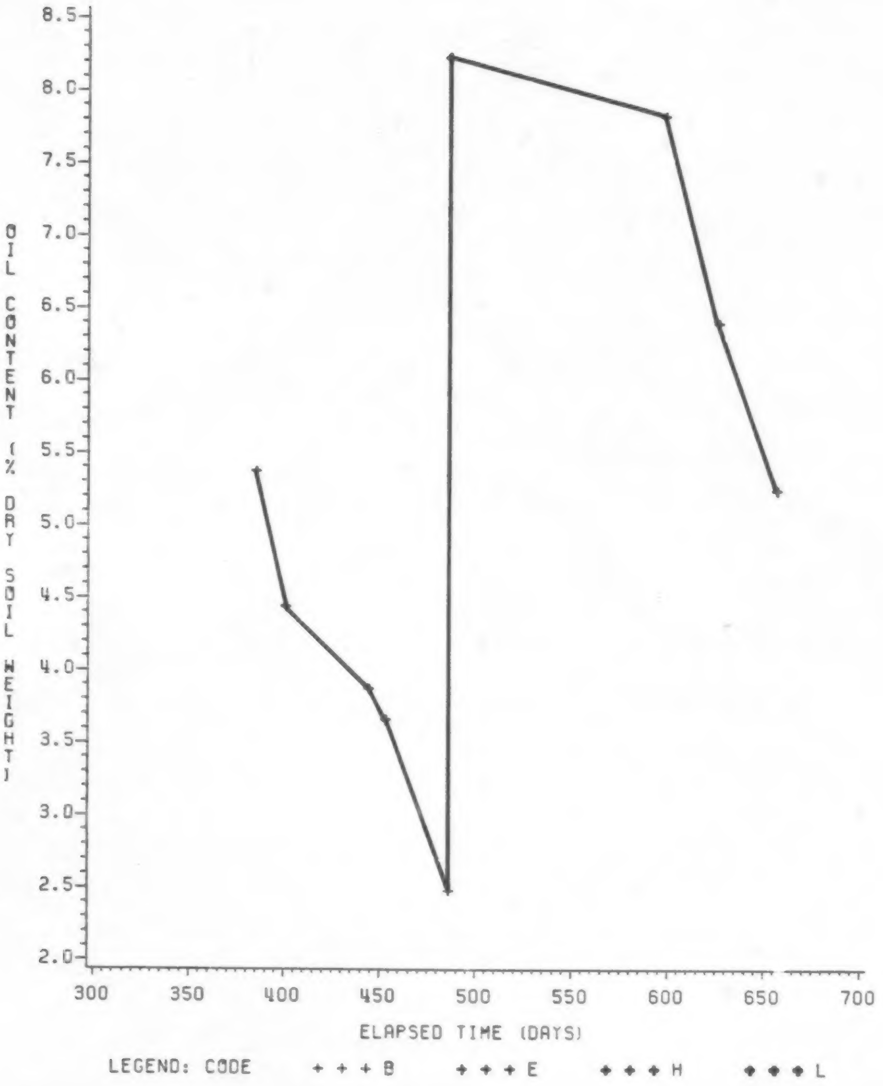

Figure A.30. Time series oil content history, plot 35.

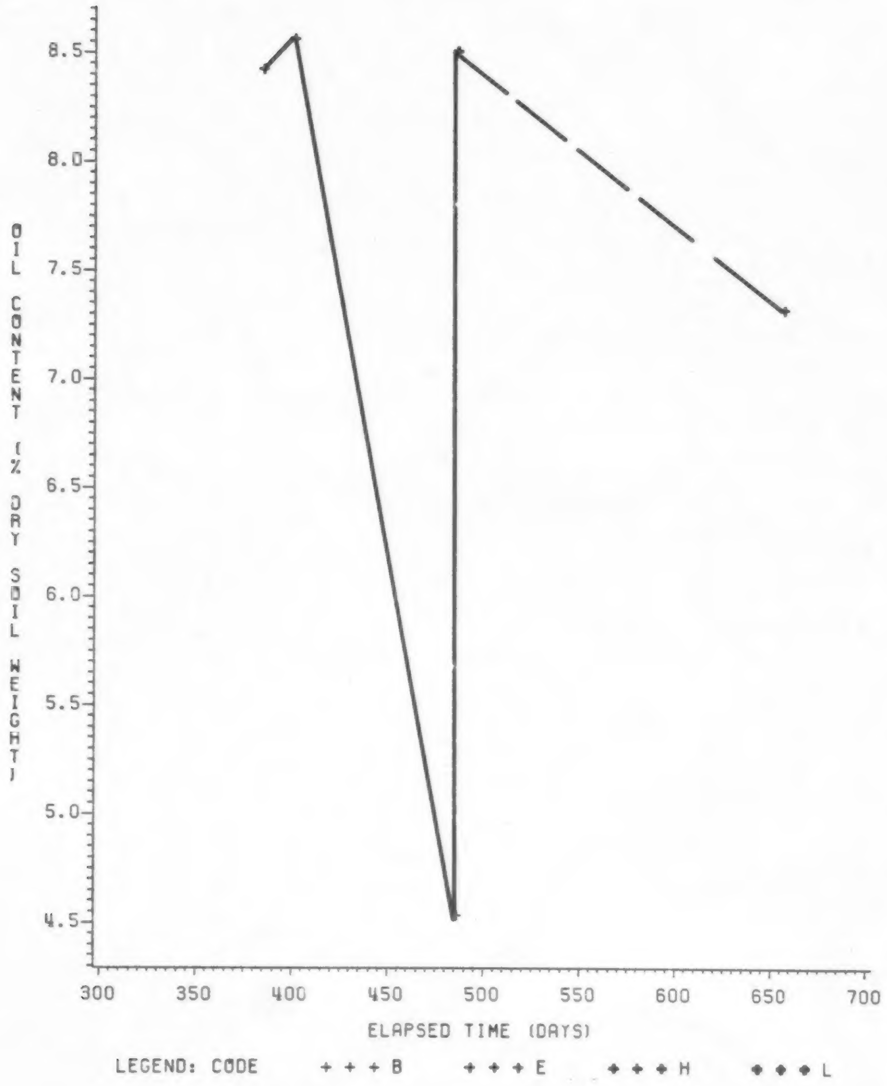

Figure A.31. Time series oil content history, plot 36.

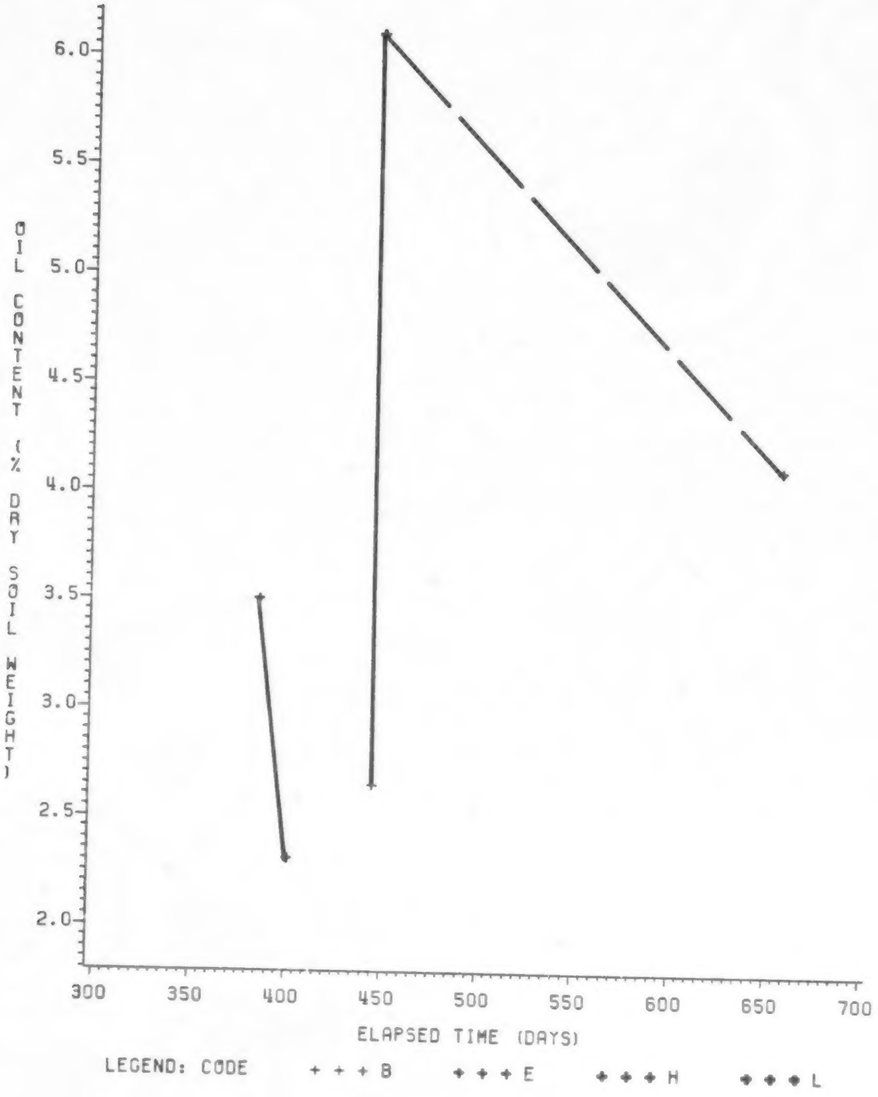

Figure A.32. Time series oil content history, plot 38.

APPENDIX B

VOLATILE EMISSIONS DATA

TABLE B.1. CALCULATED EMISSION RATES OF TOTAL VOLATILE HYDROCARBONS FOR FIELD EXPERIMENTS

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
07/19/82	1	13	AT	7.90	.	.	90	57
07/19/82	1	13	AA1	118.47	.	.	91	54
07/19/82	1	13	IAT,AA	96.89	.	27.4	91	54
07/20/82	1	13	BETA	24.57	.	.	90	57
07/21/82	1	13	BETA	14.90	.	.	85	58
08/02/82	1	13	BETA	11.70	.	.	92	58
08/17/82	1	13	BT	7.90	.	.	87	66
08/17/82	1	13	AT	13.16	.	.	87	66
08/17/82	1	13	AA2	38.89	8	.	83	65
08/17/82	1	13	5AA	21.45	.	24.9	87	66
08/17/82	1	13	IAT,AA	19.50	.	24.9	91	75
08/17/82	1	13	20AT,AA	19.50	.	24.9	91	76
08/28/82	1	13	BETA	12.43	.	20.5	87	35
08/31/82	1	13	BETA	11.70	.	20.0	84	38
09/01/82	1	13	AT	18.25	.	18.1	93	20
09/02/82	1	13	90AT	16.33	.	17.5	91	21
09/09/82	1	13	120AT	15.68	.	15.4	91	48
09/10/82	1	13	BETA	11.70	.	.	76	49
09/10/82	1	13	AA3	35.10	8	.	75	56
09/10/82	1	13	IAT,AA	40.22	.	.	64	85
09/11/82	1	13	BETA	19.83	.	.	86	62
09/21/82	1	13	BETA	13.15	.	.	87	61
10/07/82	1	13	BT	10.81	.	.	85	40
10/07/82	1	13	AT	17.55	.	.	90	45
10/14/82	1	13	BETA	11.70	.	.	84	60
10/14/82	1	13	BETA	18.65	.	.	84	61
10/14/82	1	13	AA4	409.52	14	.	84	62
10/14/82	1	13	IAT,AA	190.14	.	29.7	83	73
10/15/82	1	13	BETA	57.51	.	.	80	65
10/17/82	1	13	BETA	25.26	.	.	79	65
10/21/82	1	13	BT	16.09	.	23.1	75	35
10/21/82	1	13	AT	39.49	.	24.0	76	71
10/28/82	1	13	BETA	11.70	.	21.0	72	31
11/02/82	1	13	BT	11.70	.	.	69	35
11/02/82	1	13	AT,BA	38.66	.	.	68	38
11/02/82	1	13	AA5	367.69	13	.	69	77
11/02/82	1	13	IAT,AA	402.51	.	.	77	85
11/02/82	1	13	2HA,AT	325.15	.	.	77	85
11/02/82	1	13	4HA,AT	255.26	.	.	77	84
11/02/82	1	13	6HA,AT	199.28	.	.	77	84
11/03/82	1	13	BETA	65.01	.	.	75	90
11/05/82	1	13	BETA	29.25	.	.	68	61
11/09/82	1	13	BETA	26.33	.	.	65	58
11/17/82	1	13	BT	10.82	.	28.8	50	60
11/17/82	1	13	AT	15.15	.	28.8	55	84
11/17/82	1	13	AA6	72.57	9	.	55	84
11/17/82	1	13	30AT,AA	62.77	.	.	50	85
11/17/82	1	13	4HRAA,A	35.11	.	.	50	82
11/18/82	1	13	24HA,AA	15.13	.	.	51	70
11/24/82	1	13	BETA	5.85	.	.	44	50
12/20/82	1	13	BETA	3.21	.	.	41	43
07/20/82	6	13	BA	7.90	.	.	90	56
07/20/82	6	13	AA1	112.50	.	.	90	56
07/20/82	6	13	AT,AA	96.87	.	.	90	56
07/21/82	6	13	BETA	24.57	.	.	81	55
07/25/82	6	13	BETA	11.90	.	.	82	50
08/08/82	6	13	BETA	5.12	.	17.3	91	35
08/09/82	6	13	BETA	5.12	.	17.2	105	39
08/10/82	6	13	BETA	5.12	.	17.0	103	63

(continued)

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TABLE B.1. (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
08/10/82	6	13	BETA	11.70	.	18.4	106	68
08/17/82	6	13	BETA	11.70	.	.	87	65
08/17/82	6	13	AA2	35.89	8	.	89	72
08/17/82	6	13	1.5HRAT	21.45	.	23.9	89	71
08/26/82	6	13	BETA	6.82	.	20.5	92	39
08/31/82	6	13	BETA	6.82	.	19.0	89	31
09/01/82	6	13	.5HR AT	18.28	.	18.1	94	31
09/02/82	6	13	1.5HR A	15.67	.	17.7	94	31
09/09/82	6	13	BETA	6.65	.	.	88	52
09/09/82	6	13	1.5 AT	17.55	.	.	89	53
09/10/82	6	13	AA3	35.10	8	.	82	60
09/10/82	6	13	IAT,AA	40.22	.	.	82	60
09/11/82	6	13	BETA	19.83	.	.	86	61
09/21/82	6	13	BETA	13.16	.	.	87	62
10/07/82	6	13	BETA	10.24	.	.	88	45
10/07/82	6	13	IAT,BA	13.16	.	.	88	52
10/14/82	6	13	BETA	9.51	.	.	80	35
10/14/82	6	13	IAT,BA	13.16	.	.	81	37
10/14/82	6	13	AA4	398.90	.	.	80	81
10/14/82	6	13	IAT,AA	116.99	14	22.4	80	81
10/15/82	6	13	BETA	45.67	.	22.1	80	81
10/17/82	6	13	BETA	24.82	.	.	69	60
10/21/82	6	13	BETA	14.62	.	.	66	58
10/21/82	6	13	BA,AT	39.48	.	.	65	58
10/25/82	6	13	BT	11.70	.	.	70	59
11/02/82	6	13	BA	10.23	.	.	65	60
11/02/82	6	13	AT	34.59	.	.	65	62
11/02/82	6	13	IAP,BT	337.83	13	.	69	77
11/02/82	6	13	IAT,AA	401.30	.	.	69	85
11/03/82	6	13	BETA	64.58	.	.	59	75
11/05/82	6	13	BETA	29.95	.	.	62	78
11/09/82	6	13	BT	23.40	.	.	69	80
11/17/82	6	13	BT	11.70	.	28.5	50	60
11/17/82	6	13	AT,BA	13.65	.	28.5	53	65
11/17/82	6	13	AA	69.90	.	.	52	86
11/17/82	6	13	IAT,AA	54.59	9	.	50	85
11/24/82	6	13	BT	5.85	.	.	44	50
12/20/82	6	13	BT	3.90	.	.	40	43
07/13/82	5	10	BA	4.39	.	.	95	60
07/13/82	5	10	AT,BA	11.70	.	.	95	60
07/13/82	5	10	AA	98.51	.	.	95	62
08/06/82	5	10	BT,BA	5.85	.	.	104	23
08/10/82	5	10	BT,BA	4.39	.	.	95	62
08/10/82	5	10	IAT,BA	11.70	.	18.7	97	68
08/12/82	5	10	BT,BA	5.12	.	.	97	63
08/12/82	5	10	IAA	66.55	9	.	102	64
08/12/82	5	10	IAT,AA	38.39	.	20.1	102	64
08/25/82	5	10	BT	7.80	.	.	95	39
08/31/82	5	10	BT	5.85	.	.	97	36
09/01/82	5	10	IAT,BA	23.15	.	.	96	45
09/02/82	5	10	IAT	17.55	.	.	83	67
09/09/82	5	10	BT	5.85	.	.	80	38
09/09/82	5	10	IAT,BA	14.63	.	10.5	89	72
09/23/82	5	10	BT,BA	5.85	.	15.7	63	40
09/23/82	5	10	IAT,BA	12.40	.	.	65	41
09/23/82	5	10	IAA,BT	394.90	14	.	72	60
09/23/82	5	10	IAT,AA	453.40	.	.	74	67
09/23/82	5	10	2-HR AA	255.12	.	.	74	65
09/23/82	5	10	4HR AA	179.40	.	.	74	65

(continued)

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TABLE B.1. (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
09/24/82	5	10	BETA	61.24	.	.	70	.
09/26/82	5	10	BETA	31.17	.	.	75	58
10/07/82	5	10	BT	17.55	.	.	84	56
10/07/82	5	10	IAT,BA	61.43	.	16.2	91	58
10/12/82	5	10	BT,BA	11.70	.	.	90	59
10/12/82	5	10	IAT,AA	175.51	13	.	91	62
10/21/82	5	10	BT,BA	16.09	.	.	73	37
10/21/82	5	10	IAT,BA	51.19	.	.	73	61
10/25/82	5	10	BT,BA	15.95	.	.	64	39
11/02/82	5	10	BT,BA	16.09	.	.	66	45
11/02/82	5	10	AT,BA	23.64	.	.	67	46
11/02/82	5	10	5AA,BT	248.64	13	.	67	79
11/02/82	5	10	60AT	162.35	.	.	75	56
11/02/82	5	10	2HA AT	107.12	.	.	75	64
11/02/82	5	10	4HA AT	71.29	.	.	76	64
11/03/82	5	10	BETA	45.21	.	.	78	70
11/05/82	5	10	BETA	27.89	.	.	73	71
11/09/82	5	10	BT,BA	16.09	.	.	69	65
11/09/82	5	10	IAT,BA	24.13	.	.	69	68
11/17/82	5	10	BT	10.01	.	.	64	68
11/17/82	5	10	AT,BA	32.99	.	.	64	88
11/17/82	5	10	IAT,AA	101.74	12	.	64	92
11/17/82	5	10	2HA AA	63.21	.	.	65	85
11/17/82	5	10	4HA AA	41.24	.	.	65	85
11/18/82	5	10	BETA	14.98	.	.	53	72
11/24/82	5	10	BT,BA	6.83	.	.	49	43
12/20/82	5	10	BT,BA	3.90	.	.	51	31
07/20/82	7	6	BT,BA	3.22	.	.	73	44
07/20/82	7	6	IAA,BT	60.24	.	.	85	37
07/20/82	7	6	IAT,AA	53.24	.	.	88	40
08/05/82	7	6	BT,BA	5.85	.	.	107	25
08/09/82	7	6	BT,BA	5.85	.	.	98	24
08/10/82	7	6	BT,BA	3.90	.	.	96	58
08/10/82	7	6	30AT,BA	7.80	.	20.7	97	60
08/17/82	7	6	BT,BA	3.90	.	.	80	50
08/17/82	7	6	AT,BA	7.80	.	.	80	50
08/17/82	7	6	AA	27.30	8	.	62	54
08/17/82	7	6	IAT,AA	18.53	.	18.4	85	74
08/26/82	7	6	BT,BA	5.85	.	.	87	33
08/31/82	7	6	BT,BA	5.85	.	.	89	31
09/01/82	7	6	AT,BA	23.40	.	.	90	26
09/02/82	7	6	30AT,BA	17.55	.	.	86	51
09/09/82	7	6	180AT	13.16	.	6.9	85	58
09/23/82	7	6	BA	5.85	.	.	72	51
09/23/82	7	6	AA	350.09	14	.	72	51
09/23/82	7	6	IAA,AT	385.95	.	.	72	51
10/07/82	7	6	BA	11.85	.	.	82	55
10/07/82	7	6	IAT,BA	17.55	.	14.3	82	56
10/12/82	7	6	BT,BA	5.85	.	.	75	58
10/12/82	7	6	IAT,AA	1170.07	14	.	74	59
10/21/82	7	6	BT,BA	11.70	.	.	62	39
10/21/82	7	6	AT,BA	36.56	.	.	53	53
10/26/82	7	6	BT,BA	7.31	.	.	62	37
11/02/82	7	6	BT,BA	4.33	.	.	69	37
11/09/82	7	6	BT,BA	4.33	.	.	69	39
11/17/82	7	6	BT,BA	4.33	.	15.7	50	83
11/17/82	7	6	AT,BA	15.15	.	15.7	47	88
11/17/82	7	6	AA,BT	67.10	9	.	50	93
11/17/82	7	6	60AT,AA	28.14	.	.	50	83

(continued)

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TABLE B.1. (continued)

Date of Sampling	Plot No.	Nominal Loading Rate (%)	Sampling* Status	Rate of Emis. (g/hr)	Vola. of Slud. (%)	Soil Mois. Cont. (%)	Soil Temp. (°F)	Rela. Humid. (%)
11/24/82	7	6	BT,BA	5.85	.	.	48	45
12/20/82	7	6	BT,BA	2.93	.	.	55	25
07/13/82	4	3	BT,BA	3.22	.	.	90	57
07/13/82	4	3	AA	35.57	.	.	90	56
07/13/82	4	3	IAT	24.57	.	.	90	56
08/06/82	4	3	BT,BA	5.85	.	.	98	23
08/10/82	4	3	AT,BA	14.62	.	27.0	68	74
08/13/82	4	3	AA,BT	42.90	8	.	63	62
08/13/82	4	3	AT,AA	30.22	.	17.0	65	57
08/26/82	4	3	BT,BA	2.92	.	.	87	32
08/31/82	4	3	BT,BA	2.92	.	.	67	27
09/09/82	4	3	BT,BA	2.92	.	.	79	33
09/09/82	4	3	20AT,BA	14.62	.	6.3	81	33
09/23/82	4	3	BT,BA	3.80	.	13.4	71	40
09/23/82	4	3	AT,BA	12.54	.	13.9	71	42
09/23/82	4	3	AT,AA	190.11	14	.	71	65
10/07/82	4	3	BT,BA	5.85	.	.	78	53
10/07/82	4	3	AT,BA	16.09	.	11.5	79	52
10/12/82	4	3	BT,BA	4.39	14	.	67	43
10/12/82	4	3	60AA	116.99	14	.	68	63
10/12/82	4	3	AT,AA	51.18	14	.	72	65
10/21/82	4	3	AT,BA	21.20	14	.	63	70
10/22/82	4	3	BT,BA	13.16	14	.	63	38
10/26/82	4	3	BT,BA	4.39	14	.	57	38
11/02/82	4	3	BT,BA	4.39	14	.	59	52
11/02/82	4	3	AT,BA	12.54	14	.	59	55
11/02/82	4	3	15AA,BT	233.98	13	.	61	73
11/02/82	4	3	35AT,AA	145.09	13	.	64	74
11/09/82	4	3	BT,BA	8.66	13	.	68	70
11/09/82	4	3	AT,BA	15.15	13	.	69	78
11/17/82	4	3	BT,BA	5.85	13	.	69	71
11/17/82	4	3	AT,BA	12.99	13	13.3	49	62
11/17/82	4	3	AT,AA	32.46	9	.	50	69
11/24/82	4	3	BT,BA	5.85	9	.	45	41
12/20/82	4	3	BT,BA	2.93	9	.	52	29

* AT = After Tilling, AA = After Application,
IAT = Immediately After Tilling, BT = Before Tilling,
BETA = Between Two Application, BA = Before Application,
20 AT = 20 Min. After Tilling, 90 AT = 90 Min. After Tilling,
2 HR AA = 2 Hours After Application

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TABLE B.2. CALCULATED EMISSION RATES OF TOTAL VOLATILE HYDROCARBONS FOR LABORATORY EXPERIMENTS

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (^oF)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
06/01/83	0.033	3	511.906	85	52	12	8.5
06/01/83	0.066	3	477.779	85	52	12	8.5
06/01/83	0.083	3	392.461	85	52	12	8.5
05/01/83	0.166	3	341.270	85	52	12	8.5
06/01/63	0.750	3	136.506	85	52	12	8.5
06/01/63	3.000	3	59.722	85	52	12	8.5
06/02/63	24.000	3	25.595	85	52	12	8.5
06/03/83	48.000	3	23.595	85	52	12	8.5
06/03/93	48.500	3	58.015	85	52	12	8.5
06/04/83	72.000	3	13.650	85	52	12	8.5
05/05/93	96.000	3	12.790	85	52	12	8.5
06/08/83	168.000	3	12.790	85	52	12	8.5
06/08/83	166.500	3	42.658	85	52	12	6.5
06/09/83	192.000	3	14.620	85	52	12	8.5
06/01/83	0.033	6	546.033	85	52	12	8.5
06/01/93	0.066	6	546.033	85	52	12	8.5
06/01/63	0.166	6	392.450	85	52	12	8.5
06/01/83	0.416	6	238.889	85	52	12	6.5
06/01/83	0.750	6	170.638	85	52	12	8.5
06/01/83	1.330	6	136.508	85	52	12	8.5
06/01/83	3.500	6	76.785	85	52	12	9.5
06/01/83	4.250	6	68.254	85	52	12	8.5
06/02/83	24.000	6	28.154	85	52	12	8.5
06/03/63	48.000	6	25.595	85	52	12	8.5
06/03/83	48.500	6	63.135	85	52	12	8.5
06/04/83	72.000	6	23.876	85	52	12	8.5
06/08/83	168.000	6	21.938	85	52	12	8.5
05/08/83	168.500	6	46.315	85	52	12	8.5
05/09/83	192.000	6	30.710	85	52	12	8.5
06/03/83	0.033	10	590.150	85	52	12	8.5
05/03/83	0.066	10	580.150	85	52	12	8.5
06/03/63	0.166	10	460.715	85	52	12	8.5
06/03/83	1.000	10	307.143	85	52	12	8.5
06/03/83	1.500	10	255.953	85	52	12	8.5
06/03/63	3.000	10	153.570	85	52	12	6.5
06/03/83	6.500	10	110.913	85	52	12	8.5
06/04/83	24.000	10	42.657	85	52	12	8.5
06/08/93	120.000	10	28.030	85	52	12	8.5
06/08/83	120.500	10	59.722	85	52	12	8.5
06/09/63	144.000	10	24.161	85	52	12	8.5
06/10/83	168.000	10	14.626	85	52	12	8.5
06/10/83	168.500	10	43.721	85	52	12	8.5
05/10/83	172.000	10	32.215	85	52	12	6.5
06/11/83	192.000	10	15.720	85	52	12	8.5
05/16/83	0.033	3	307.144	60	52	12	6.5
05/16/83	0.066	3	307.144	60	52	12	8.5
05/15/83	0.165	3	255.953	60	52	12	6.5
05/16/83	0.330	3	213.294	60	52	12	8.5
05/16/83	0.500	3	187.699	60	52	12	8.5
05/16/83	0.666	3	170.635	60	52	12	8.5
05/16/83	0.833	3	153.571	60	52	12	9.5
05/15/83	1.000	3	153.571	60	52	12	8.5
05/16/83	3.000	3	61.428	60	52	12	9.5
05/16/63	5.000	3	37.539	60	52	12	8.5
05/17/63	24.000	3	18.769	60	52	12	8.5
05/18/83	48.000	3	5.210	60	52	12	9.5
05/16/83	46.500	3	32.420	60	52	12	8.5
05/18/83	49.000	3	30.719	60	52	12	8.5
05/19/83	72.000	3	15.357	60	52	12	8.5

(continued)

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TABLE B.2 (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (^{o}F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
05/20/83	96.000	3	10.238	60	52	12	8.5
05/20/83	96.500	3	23.888	60	52	12	8.5
05/20/83	98.000	3	14.504	60	52	12	8.5
05/20/83	101.000	3	14.504	60	52	12	8.5
05/21/83	120.000	3	10.238	60	52	12	8.5
05/22/83	144.000	3	7.676	60	52	12	8.5
05/17/83	0.033	6	375.397	60	52	12	8.5
05/17/83	0.066	6	341.270	60	52	12	8.5
05/17/83	0.166	6	255.953	60	52	12	8.5
05/17/83	0.333	6	221.826	60	52	12	8.5
05/17/83	0.500	6	204.762	60	52	12	8.5
05/17/83	0.750	6	196.230	60	52	12	8.5
05/17/83	0.833	6	187.698	60	52	12	8.5
05/17/83	1.000	6	162.103	60	52	12	8.5
05/17/83	4.000	6	59.722	60	52	12	8.5
05/17/83	6.000	6	37.500	60	52	12	8.5
05/18/83	22.000	6	25.595	60	52	12	8.5
05/18/83	24.000	6	20.476	60	52	12	8.5
05/19/83	48.000	6	20.476	60	52	12	8.5
05/19/83	48.500	6	54.603	60	52	12	8.5
05/19/83	49.010	6	51.190	60	52	12	8.5
05/19/83	53.000	6	34.127	60	52	12	8.5
05/20/83	72.000	6	20.476	60	52	12	8.5
05/21/83	96.000	6	11.944	60	52	12	8.5
05/21/83	96.500	6	32.420	60	52	12	8.5
05/22/83	120.000	6	13.650	60	52	12	8.5
05/23/83	144.000	6	8.531	60	52	12	8.5
05/24/83	0.033	10	375.394	50	52	12	8.5
05/24/83	0.166	10	307.143	60	52	12	8.5
05/24/83	0.333	10	273.016	60	52	12	8.5
05/24/83	0.500	10	255.953	60	52	12	8.5
05/24/83	0.750	10	238.889	60	52	12	8.5
05/24/83	1.000	10	230.357	60	52	12	8.5
05/24/83	1.750	10	213.294	60	52	12	8.5
05/24/83	4.000	10	170.635	60	52	12	8.5
05/24/83	5.000	10	133.095	60	52	12	8.5
05/25/83	21.000	10	29.008	60	52	12	8.5
05/25/83	24.000	10	27.813	60	52	12	8.5
05/26/83	48.000	10	26.448	60	52	12	8.5
05/26/83	48.500	10	88.730	60	52	12	8.5
05/26/83	49.010	10	81.904	60	52	12	8.5
05/26/83	54.000	10	30.714	60	52	12	8.5
05/27/83	72.000	10	23.888	60	52	12	8.5
05/28/83	96.000	10	11.944	60	52	12	8.5
05/28/83	96.500	10	47.777	60	52	12	8.5
05/29/83	120.000	10	13.650	60	52	12	8.5
05/30/83	144.000	10	11.051	60	52	12	8.5
03/31/83	0.033	3	204.762	35	52	12	8.5
03/31/83	0.083	3	170.635	35	52	12	8.5
03/31/83	1.000	3	127.976	35	52	12	8.5
03/31/83	2.000	3	119.444	35	52	12	8.5
03/31/83	4.000	3	40.952	35	52	12	8.5
03/31/83	6.000	3	32.761	35	52	12	8.5
03/31/83	8.000	3	29.008	35	52	12	8.5
04/01/83	24.000	3	13.650	35	52	12	8.5
04/02/83	48.000	3	5.972	35	52	12	8.5
04/02/83	48.500	3	22.182	35	52	12	8.5
04/03/83	72.000	3	13.650	35	52	12	8.5
04/03/83	74.000	3	11.944	35	52	12	8.5

(continued)

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TABLE B.2. (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (^{o}F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
04/03/83	78.000	3	11.944	35	52	12	8.5
04/04/83	96.000	3	8.531	35	52	12	8.5
04/04/83	96.500	3	20.476	35	52	12	8.5
04/04/83	99.000	3	15.357	35	52	12	8.5
04/04/83	101.000	3	11.944	35	52	12	8.5
04/05/83	120.000	3	8.531	35	52	12	8.5
04/06/83	144.000	3	5.972	35	52	12	8.5
04/04/83	0.033	6	307.143	35	52	12	8.5
04/04/83	0.166	6	238.889	35	52	12	8.5
04/04/83	0.500	6	187.698	35	52	12	8.5
04/04/83	0.750	6	153.571	35	52	12	8.5
04/04/83	2.000	6	136.508	35	52	12	8.5
04/04/83	4.000	6	54.603	35	52	12	8.5
04/04/83	6.000	6	42.658	35	52	12	8.5
04/04/83	8.000	6	23.888	35	52	12	8.5
04/05/83	24.000	6	17.063	35	52	12	8.5
04/06/83	48.000	6	10.238	35	52	12	8.5
04/06/83	48.500	6	35.833	35	52	12	8.5
04/07/83	72.000	6	12.797	35	52	12	8.5
04/08/83	96.000	6	10.238	35	52	12	8.5
04/08/83	96.500	6	34.127	35	52	12	8.5
04/09/83	120.000	6	6.825	35	52	12	8.5
04/10/83	144.000	6	5.119	35	52	12	8.5
04/01/83	0.033	10	238.889	35	52	12	8.5
04/01/83	0.083	10	204.762	35	52	12	8.5
04/01/83	0.500	10	170.635	35	52	12	8.5
04/01/83	1.000	10	127.979	35	52	12	8.5
04/01/83	5.000	10	40.952	35	52	12	8.5
04/01/83	8.000	10	34.127	35	52	12	8.5
04/02/83	24.000	10	22.182	35	52	12	8.5
04/03/83	48.000	10	11.944	35	52	12	8.5
04/03/83	48.500	10	39.246	35	52	12	8.5
04/04/83	72.000	10	13.650	35	52	12	8.5
04/05/83	96.000	10	11.944	35	52	12	8.5
04/05/83	96.500	10	35.833	35	52	12	8.5
04/06/83	120.000	10	10.238	35	52	12	8.5
04/07/83	144.000	10	8.531	35	52	12	8.5
06/10/83	0.033	6	511.906	60	52	23	8.5
06/10/83	0.066	6	477.779	60	52	23	8.5
06/10/83	0.166	6	375.397	60	52	23	8.5
06/10/83	0.250	6	307.143	60	52	23	8.5
06/10/83	1.000	6	280.083	60	52	23	8.5
06/10/83	2.000	6	240.550	60	52	23	8.5
06/10/83	4.000	6	204.762	60	52	23	8.5
06/10/83	6.000	6	127.979	60	52	23	8.5
06/10/83	24.000	6	54.603	60	52	23	8.5
06/12/83	48.000	6	40.952	60	52	23	8.5
06/12/83	48.500	6	64.841	60	52	23	8.5
06/13/83	72.000	6	37.539	60	52	23	8.5
06/14/83	96.000	6	34.127	60	52	23	8.5
06/14/83	96.500	6	50.337	60	52	23	8.5
06/15/83	120.000	6	34.127	60	52	23	8.5
06/16/83	144.000	6	30.714	60	52	23	8.5
07/05/83	0.033	6	341.270	60	75	12	8.5
07/05/83	0.083	6	290.080	60	75	12	8.5
07/05/83	0.166	6	204.760	60	75	12	8.5
07/05/83	0.333	6	170.630	60	75	12	8.5
07/05/83	1.000	6	124.550	60	75	12	8.5
07/05/83	3.000	6	30.710	60	75	12	8.5

(continued)

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TABLE B.2. (continued)

Date of Sampling	Time Since Appl. (hr.)	Loading Rate (%)	Rate of Emission (g/hr)	Soil Temp. (^{o}F)	Rela. Humid. (%)	Soil Mois. Cont. (%)	Vola. of Slud. (%)
07/05/83	6.000	6	27.300	60	75	12	6.5
07/06/83	24.000	6	15.350	60	75	12	6.5
07/07/83	48.000	6	10.230	60	75	12	6.5
07/07/83	48.500	6	19.620	60	75	12	6.5
07/08/83	72.000	6	10.230	60	75	12	6.5
07/09/83	96.000	6	6.820	60	75	12	6.5
07/09/83	96.500	6	14.500	60	75	12	6.5
07/10/83	120.000	6	8.530	60	75	12	6.5
07/11/83	145.000	6	5.110	60	75	12	6.5
07/05/83	0.033	10	341.270	60	75	12	6.5
07/05/83	0.166	10	238.890	60	75	12	6.5
07/05/83	0.333	10	204.760	60	75	12	6.5
07/05/83	0.500	10	195.230	60	75	12	6.5
07/05/83	1.000	10	153.570	60	75	12	6.5
07/05/83	4.000	10	93.940	60	75	12	6.5
07/05/83	6.000	10	76.790	60	75	12	6.5
07/06/83	24.000	10	18.760	60	75	12	6.5
07/07/83	48.000	10	14.500	60	75	12	6.5
07/07/83	48.500	10	23.880	60	75	12	6.5
07/08/83	72.000	10	15.350	60	75	12	6.5
07/09/83	96.000	10	10.230	60	75	12	6.5
07/09/83	96.500	10	20.470	60	75	12	6.5
07/10/83	120.000	10	11.940	60	75	12	6.5
07/11/83	146.000	10	8.530	60	75	12	6.5

* Soil and sludge mixture was tilled.

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TABLE B.3. THE TOTAL VOLATILE EMISSION MODELS FOR FIELD DATA

1. Model 1 Time <10 hours
Dependent Variable: Emission Rate

$R^2 = .83$, F Value = 27.49

Independent Variables	Estimate	T for Ho: Independent Variables = 0	Probability |t| Cal.>|t|tab.*	Standard Error of Estimate
Intercept	76.594	1.48	.1508	51.849
Soil Temperature	.769	1.77	.0874	.434
Moisture Content	8.828	5.08	.0001	1.737
Time Since Application	-20.645	-7.35	.0001	2.810
Loading Rate	9.985	4.31	.0002	2.316
Relative Humidity	-2.025	-2.81	.0090	.721

2. Model 2 Time <10 hours
Dependent Variable: Emission Rate

$R^2 = .76$, F Value = 49.83

Intercept	.184	.04	.9716	5.163
Soil Temperature	.268	8.18	.0001	.032
Moisture Control	1.879	9.67	.0001	.194
Time Since Application	-.084	-7.15	.0001	.011
Loading Rate	.931	4.51	.0001	.206
Relative Humidity	-.371	-5.26	.0001	.070

* Ho is rejected if the probability |t| cal.> |t| tab. >95%.

TABLE B.4. EMISSION RATES OF MEASURED HYDROCARBONS

Temp = 85, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	.033	.166	1.0	3	24	48	48.5*	96	168	168.5*
COMPOUND NAME				GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)						
1. PENTANE	0.416	0.397	0.29	0.018	0.003	0.006	0.007	0.005	0.012	0.021
2. CYCLOPENTANE	0.916	0.935	0.959	0.47	0.107	0.105	0.361	0.56	0.53	0.865
3. HEXANE	6.878	4.508	1.194	0.313	0.204	0.027	0.033	0.019	0.018	0.025
4. METHYL CYCLOPENTANE	3.594	2.26	3.16	0.27	0.036	0.073	0.252	0.051	0.201	0.672
5. BENZENE	2.6	2.212	3.615	0.314	0.074	0.069	0.364	0.073	0.269	0.824
6. 2,4-DIMETHYLPENTANE	16.7	12.811	4.544	1.707	0.153	0.159	0.288	0.055	0.047	0.067
7. CYCLOHEXANE	4.272	2.828	1.272	0.262	0.023	0.016	0.077	0.069	0.05	0.119
8. 3-METHYLHEXANE	8.839	7.963	2.311	0.764	0.248	0.206	0.291	0.074	0.107	0.54
9. METHYLCYCLOHEXANE	7.252	4.746	4.759	1.465	0.398	0.21	0.316	0.088	0.036	0.417
10. 2,5-DIMETHYLHEXANE	7.871	6.511	2.984	0.967	0.682	0.427	0.794	0.274	0.124	0.349
11. 2,3,4-TRIMETHYLPENTANE	33.018	26.696	10.255	3.527	1.382	0.728	1.012	0.394	0.234	0.471
12. 3-METHYLHEPTANE	7.218	3.972	2.345	0.856	0.426	0.386	1.632	0.388	0.246	0.988
13. 2,2,5-TRIMETHYLHEXANE	4.687	4.279	3.259	1.284	0.714	0.672	1.479	0.587	0.419	0.529
14. 1,4-DIMETHYLBENZENE	5.326	5.203	3.642	1.546	1.374	1.295	2.472	0.996	0.988	1.458
SUM OF 14 COMPOUNDS	109.587	85.321	44.589	13.763	5.824	4.379	9.368	3.636	3.281	7.345
TOTAL VOLAT. AS HEXANE	477.779	341.270	136.508	59.722	25.595	23.095	58.016	12.790	12.793	42.658
% 14 COMP/TOTAL VOLAT	22.94	25.00	32.66	23.05	22.75	18.96	16.15	28.43	25.65	17.22

* SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.5. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp. = 85, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.033	.166	.50	1	5	24	48	48.5*	168	168.5*	192
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)										
1. PENTANE	0.382	0.342	0.336	0.0167	.	.	.	0.022	0.0405	0.095	0.006
2. CYCLOPENTANE	0.402	0.46	0.11	0.078	0.04	0.058	0.021	1.34	0.945	0.946	0.172
3. HEXANE	8.848	7.419	2.19	1.006	0.314	0.1836	0.018	0.08	0.017	0.113	0.02
4. METHYL CYCLOPENTANE	4.42	3.66	3.304	0.524	0.168	0.135	0.1021	0.598	0.26	0.382	0.048
5. BENZENE	2.694	2.45	2.168	0.453	0.204	0.161	0.09	0.742	0.372	0.52	0.084
6. 2,4-DIMETHYLPENTANE	20.156	20.085	11.906	4.97	1.86	0.197	0.104	0.194	0.038	0.052	0.046
7. CYCLOHEXANE	5.388	4.708	2.098	0.793	0.21	0.086	0.051	0.098	0.068	0.193	0.02
8. 3-METHYLHEXANE	10.002	9.711	3.685	2.496	1.074	0.3939	0.479	0.268	0.042	0.083	0.04
9. METHYLCYCLOHEXANE	8.254	6.773	6.147	1.249	0.514	0.128	0.074	0.698	0.0375	0.047	0.028
10. 2,5-DIMETHYLHEXANE	9.988	9.345	4.207	3.195	1.448	0.264	0.198	0.666	0.091	0.095	0.81
11. 2,3,4-TRIMETHYLPENTANE	34.968	33.365	16.009	11.836	3.554	1.438	0.324	1.114	0.15	0.45	0.18
12. 3-METHYLHEPTANE	8.104	8.676	4.609	4.287	1.65	0.376	0.169	0.594	0.331	1.082	0.324
13. 2,2,5-TRIMETHYLHEXANE	4.49	4.304	2.318	2.247	1.19	0.387	0.23	0.95	0.245	0.646	0.466
14. 1,4-DIMETHYLBENZENE	4.08	4.718	4.555	4.062	2.624	1.341	0.552	2.516	0.433	1.928	0.582
SUM OF 14 COMPOUNDS	122.176	116.016	63.642	37.212	14.850	5.144	2.412	9.880	3.070	6.632	2.826
TOTAL VOLAT. AS HEXANE	548.000	394.480	235.889	135.508	64.284	28.154	25.598	63.135	21.938	46.415	30.710
% 14 COMP/TOTAL VOLAT	22.29	29.41	26.98	27.46	23.10	18.29	9.42	15.65	13.99	14.29	9.20

*SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.6. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 85, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.166	1.0	8.0	24	96	96.5*	192	216
COMPOUND NAME	GRAMS / HOHA / 180 SQ.FT. (PLOT AREA)							
1. PENTANE	0.394	0.166	0.006	0.03	0.026	0.036	0.022	0.032
2. CYCLOPENTANE	0.404	1.069	0.639	0.577	0.423	1.293	0.22	.
3. HEXANE	8.198	2.855	0.88	0.07	0.079	0.084	0.064	0.028
4. METHYL CYCLOPENTANE	3.88	2.355	0.756	0.844	0.44	0.816	0.074	.
5. BENZENE	2.75	1.87	0.872	1.212	0.711	1.236	0.144	0.01
6. 2,4-DIMETHYLPENTANE	21.58	9.817	3.104	0.736	0.196	0.3	0.084	0.054
7. CYCLOHEXANE	3.136	2.885	0.123	0.192	0.096	0.109	0.032	0.008
8. 3-METHYLHEXANE	11.658	5.229	1.98	0.404	0.139	0.182	0.3	0.212
9. METHYLCYCLOHEXANE	9.33	3.164	1.426	1.034	0.521	0.614	0.074	0.008
10. 2,5-DIMETHYLHEXANE	13.284	5.689	2.126	0.774	0.22	0.964	0.816	0.224
11. 2,3,4-TRIMETHTLPENTANE	46.726	22.71	7.144	2.146	0.591	1.286	0.504	0.274
12. 3-METHYLHEPTANE	9.642	5.496	3.028	0.902	0.492	0.919	1.426	0.758
13. 2,2,5-TRIMETHTLHEXANE	7.77	3.694	2.05	0.02	0.521	1.306	1.024	0.532
14. 1,4-DIMETHYLBENZENE	8.536	5.854	4.502	1.092	0.827	2.187	1.56	1.19
SUM OF 14 COMPOUNDS	147.288	72.853	28.636	10.833	5.282	11.332	6.344	3.330
TOTAL VOLAT. AS HEXANE	460.715	307.143	110.913	42.658	28.030	59.722	24.161	14.625
% 14 COMP/TOTAL VOL	31.97	23.72	25.82	25.40	18.84	18.97	26.26	22.77

* SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.7. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 60, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	.033	1.0	3.0	24	48	48.5*	72	96	96.5*	99	168
COMPOUND NAME	GRAMS / HOUR / 180 SQ. FT. (PLOT AREA)										
1. PENTANE	0.026	0.088	0.0082	0.005	0.003	0.039	0.0051	0.004	0.032	0.007	0.002
2. CYCLOPENTANE	0.082	0.356	0.102	0.104	0.06	0.032	0.057	0.2	0.43	0.298	0.058
3. HEXANE	3.766	0.657	0.436	0.007	0.006	0.28	0.019	0.008	0.036	0.008	0.001
4. METHYL CYCLOPENTANE	2.782	1.624	0.314	0.3	0.048	0.246	0.172	0.148	0.326	0.126	0.018
5. BENZENE	1.248	1.11	0.388	0.328	0.074	0.378	0.102	0.093	0.43	0.127	0.025
6. 2,4-DIMETHYLPENTANE	2.476	2.082	1.702	0.069	0.057	0.068	0.048	0.025	0.062	0.02	0.004
7. CYCLOHEXANE	1.088	1.228	0.332	0.06	0.015	0.268	0.022	0.008	0.014	0.022	0.006
8. 3-METHYLHEXANE	7.68	2.516	0.882	0.092	0.057	0.312	0.156	0.058	0.156	0.066	0.017
9. METHYLCYCLOHEXANE	5.002	4.098	0.608	0.4 .	0.066	0.252	0.148	0.1	0.464	0.152	0.024
10. 2,5-DIMETHYLHEXANE	3.202	2.642	0.94	0.152	0.102	0.592	0.262	0.06	0.2	0.434	0.138
11. 2,3,4-TRIMETHYLPENTANE	9.992	9.404	3.852	0.612	0.21	1.108	0.507	0.121	0.268	0.126	0.018
12. 3-METHYLHEPTANE	1.536	1.208	0.856	0.762	0.128	0.756	0.414	0.142	0.488	0.149	0.141
13. 2,2,5-TRIMETHYLHEXANE	3.596	1.818	0.758	.	0.105	0.708	0.315	0.122	0.368	0.167	0.094
14. 1,4-DIMETHYLBENZENE	3.68	2.187	0.806	0.4652	0.309	1.52	1.293	0.32	0.598	0.472	0.116
TOTAL VOLAT. AS HEXANE	46.156	31.108	11.984	3.356	1.240	6.559	3.520	1.409	3.872	2.174	0.662
READING FROM SNIFFER	307.144	153.571	61.428	18.769	5.210	32.420	15.357	10.238	23.838	14.504	7.678
% 14 COMP/TOTAL VOLAT	15.03	20.26	19.51	17.88	23.80	20.23	22.92	13.76	16.24	14.99	8.62

* SOIL AND SLUDGE MIXTURE WAS TILLED

TABLE B.8. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 60, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.033	6.0	24	48	48.5*	72	96	96.5*	120	146
COMPOUND NAME	GRAMS / HOUR / 180 SQ. FT. (PLOT AREA)									
1. PENTANE	0.313	0.024	0.0041	0.007	0.022	0.016	0.004	0.01	0.006	.
2. CYCLOPENTANE	0.304	0.294	0.109	0.085	0.24	0.125	0.189	0.286	0.182	0.004
3. HEXANE	5.872	0.428	0.037	0.018	0.298	0.078	0.023	0.05	0.065	.
4. METHYL CYCLOPENTANE	4.722	0.36	0.171	0.085	0.122	0.094	0.077	0.086	0.054	0.001
5. BENZENE	2.842	0.32	0.297	0.194	0.294	0.109	0.104	0.204	0.072	0.003
6. 2,4-DIMETHYLPENTANE	13.132	2.02	0.349	0.236	0.596	0.22	0.074	0.184	0.076	0.091
7. CYCLOHEXANE	1.892	0.342	0.137	0.026	0.235	0.086	0.014	0.024	0.014	0.004
8. 3-METHTLHEXANE	7.198	0.965	0.359	0.104	0.309	0.169	0.072	0.117	0.104	0.052
9. METHYLCYCLOHEXANE	6.791	0.564	0.485	0.139	0.253	0.131	0.099	0.136	0.088	0.043
10. 2,5-DIMETHYLHEXANE	5.696	0.599	0.292	0.213	0.601	0.225	0.112	0.251	0.12	0.125
11. 2,3,4-TRIMETHTLPENTANE	26.65	3.33	0.729	0.632	1.897	0.628	0.186	0.521	0.086	0.125
12. 3-METHTLHEPTANE	3.098	0.788	0.48	0.333	0.73	0.436	0.12	0.41	0.208	0.239
13. 2,2,5-TRIMETHTLHEXANE	4.314	1.318	.	0.226	0.761	0.456	0.248	0.428	0.11	.
14. 1,4-DIMETHYLBENZENE	3.738	1.372	0.539	0.427	1.168	0.544	0.29	0.655	0.36	0.33
SUM OF 14 COMPOUNDS	86.562	12.724	3.988	2.725	7.526	3.317	1.612	3.362	1.545	1.017
TOTAL VOLAT. AS HEXANE	341.270	37.510	20.476	20.376	54.603	20.476	11.944	32.420	13.650	8.531
% 14 COMP/TOTAL VOLAT	25.36	33.92	19.48	13.37	13.78	16.20	13.50	10.37	11.32	11.92

* SOIL AND SLUDGE MIXTURE WAS TILLED

TABLE B.9. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 60, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.033	.50	1.0	4	24	48	48.5*	54	72	96	96.5*	146
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)											
1. PENTANE	0.252	0.126	0.098	0.01	0.006	0.002	0.029	0.006	0.017	0.007	0.02	0.025
2. CYCLOPENTANE	0.296	0.189	0.308	0.286	0.251	0.205	0.316	0.139	0.11	0.325	0.362	0.277
3. HEXANE	6.09	3.384	2.281	2.431	0.12	0.041	1.28	0.098	0.072	0.064	0.264	0.012
4. METHYL CYCLOPENTANE	6.648	1.538	1.144	0.37	0.161	0.096	0.32	0.242	0.095	0.016	0.172	0.207
5. BENZENE	1.042	1.445	0.971	0.41	0.324	0.196	0.25	0.05	0.113	0.041	0.242	0.224
6. 2,4-DIMETHYLPENTANE	15.47	9.886	4.938	3.055	0.6	0.271	2.202	0.328	0.281	0.208	0.587	0.099
7. CYCLOHEXANE	4.014	2.036	1.644	0.535	0.393	0.035	0.248	0.142	.	0.033	0.05	0.037
8. 3-METHYLHEXANE	7.388	4.945	2.925	1.536	0.628	0.143	0.867	0.194	0.141	0.102	0.36	0.115
9. METHYLCYCLOHEXANE	6.955	2.67	2.101	0.839	0.57	0.142	0.26	0.092	0.066	0.049	0.281	0.246
10. 2,5-DIMETHYLHEXANE	6.204	4.727	2.037	1.773	0.385	0.194	1.345	0.702	0.262	0.209	0.699	0.188
11. 2,3,4-TRIMETHYLPENTANE	28.99	19.45	7.644	7.227	1.375	0.69	4.7	1.094	0.613	0.603	1.933	0.346
12. 3-METHYLHEPTANE	5.164	4.581	2.914	2.039	0.508	0.227	1.557	0.741	0.364	0.304	0.942	0.388
13. 2,2,5-TRIMETHYLHEXANE	4.606	2.335	1.304	1.272	0.704	0.369	0.98	0.78	0.348	0.251	0.625	0.416
14. 1,4-DIMETHYLBENZENE	4.667	4.141	2.86	2.263	0.883	0.548	1.565	0.834	0.517	0.99	1.215	0.616
SUM OF 14 COMPOUNDS	97.786	61.450	33.167	24.046	6.908	3.159	15.919	5.442	2.999	3.202	7.752	3.216
TOTAL VOLAT. AS HEXANE	307.143	304.016	203.000	170.635	27.813	26.448	88.730	30.774	23.868	11.841	44.000	13.650
% 14 COMP/TOTAL VOLAT	31.84	20.21	16.34	14.09	24.84	11.94	17.94	17.68	12.56	27.04	17.62	23.56

* SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.10. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 35, Loading Rate = 3%

TIME SINCE APPL. (HOURS)	2.0	6.0	48	48.5*
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)			
1. PENTANE	0.111	0.035	0.034	0.073
2. CYCLOPENTANE	0.122	0.198	0.068	0.116
3. HEXANE	0.386	0.183	0.009	0.011
4. METHYL CYCLOPENTANE	.	0.198	0.034	0.147
5. BENZENE	0.478	0.172	0.083	0.132
6. 2,4-DIMETHYLPENTANE	.	.	.	0.173
7. CYCLOHEXANE	.	.	0.029	.
8. 3-METHYLHEXANE	0.617	0.164	0.056	0.152
9. METHYLCYCLOHEXANE	0.688	0.252	0.114	0.167
10. 2,5-DIMETHYLHEXANE	0.792	0.191	0.094	0.186
11. 2,3,4-TRIMETHYLPENTANE	3.383	0.69	0.216	0.259
12. 3-METHYLHEPTANE	0.786	0.266	0.13	0.26
13. 2,2,5-TRIMETHYLHEXANE	2.398	1.609	0.1	0.214
14. 1,4-DIMETHYLBENZENE	1.287	0.573	0.192	0.38
SUM OF 14 COMPOUNDS	11.048	4.531	1.159	2.270
TOTAL VOLAT. AS HEXANE	119.000	32.761	5.972	22.182
% 14 COMP/TOTAL VOLAT	9.28	13.83	19.41	10.23

* SOIL AND SLUDGE MIXTURE WAS TILLED

TABLE B.11. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp = 35, Loading Rate = 6%

TIME SINCE APPL. (HOURS)	.50	96	146
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)		
1. PENTANE	0.236	0.085	0.039
2. CYCLOPENTANE	0.463	0.167	0.163
3. HEXANE	1.499	0.091	0.007
4. METHYL CYCLOPENTANE	1.058	0.125	0.16
5. BENZENE	1.592	0.216	0.164
6. 2,4-DIMETHYLPENTANE	5.302	0.206	0.047
7. CYCLOHEXANE	1.347	0.04	0.048
8. 3-METHYLHEXANE	3.623	0.113	0.033
9. METHYLCYCLOHEXANE	3.53	0.218	0.217
10. 2,5-DIMETHYLHEXANE	2.1	0.167	0.49
11. 2,3,4-TRIMETHYLPENTANE	8.648	0.501	0.094
12. 3-METHYLHEPTANE	2.903	0.229	0.08
13. 2,2,5-TRIMETHYLHEXANE	2.243	0.166	0.071
14. 1,4-DIMETHYLBENZENE	2.022	0.355	0.149
SUM OF 14 COMPOUNDS	36.566	2.679	1.762
TOTAL VOLAT. AS HEXANE	187.698	10.238	5.119
% 14 COMP/TOTAL VOLAT	19.48	26.17	34.42

* SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.12. EMISSION RATES OF MEASURED HYDROCARBONS BY GAS CHROMATOGRAPHY

Temp. = 35, Loading Rate = 10%

TIME SINCE APPL. (HOURS)	.033	4.0	7.0	24	48
COMPOUND NAME	GRAMS / HOUR / 180 SQ.FT. (PLOT AREA)				
1. PENTANE	0.134	0.177	0.056	0.073	0.065
2. CYCLOPENTANE	0.581	0.397	0.126	0.09	0.122
3. HEXANE	1.723	0.171	0.122	0.042	0.07
4. METHYL CYCLOPENTANE	.	0.198	0.116	0.092	0.07
5. BENZENE	0.61	0.699	0.255	0.108	0.102
6. 2,4-DIMETHYLPENTANE	.	0.722	0.581	0.333	0.245
7. CYCLOHEXANE	.	0.235	0.147	0.059	0.022
8. 3-METHYLHEXANE	4.742	0.381	0.282	0.134	0.122
9. METHYLCYCLOHEXANE	3.803	0.861	0.398	0.263	0.263
10. 2,5-DIMETHYLHEXANE	2.573	0.466	0.274	0.258	0.248
11. 2,3,4-TRIMETHYLPENTANE	8.759	1.123	0.93	0.509	0.433
12. 3-METHYLHEPTANE	3.005	0.465	0.292	0.283	0.311
13. 2,2,5-TRIMETHYLHEXANE	3.305	0.509	0.253	0.273	0.243
14. 1,4-DIMETHYLBENZENE	2.988	0.958	0.53	0.518	0.504
SUM OF 14 COMPOUNDS	32.223	7.362	4.361	3.035	2.818
TOTAL VOLAT. AS HEXANE	204.000	40.952	34.127	22.182	11.944
% 14 COMP/TOTAL VOLAT.	15.80	17.98	12.78	13.68	23.59

* SOIL AND SLUDGE MIXTURE WAS TILLED

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TABLE B.13. EMISSION RATES OF MEASURED HYDROCARBONS GAS CHROMATOGRAPHIC FIELD DATA

	Plot # 4								
	8/10/82	8/13/82		10/7/82		10/12/82	11/24/82	5/9/83	
	AT	AA	AT,AA	BT	AT	AT,AA	BT	BT	AT
Pentane	1.30	+	+	.721	6.010	.109		.026	.028
Cyclopentane	+	+	+	1.242	6.24	.790	+	.012	.204
Hexane	+	+	+	+	+	+	+	.054	.095
Methylcyclopentane	+	+	+	+	.702	.159	.802	.061	.567
Benzene	3.521	2.748	1.460	1.264	2.296	1.900	.730	.087	.569
2,4-Dimethylpentane	.060	.093	1.617	.148	.108	2.229	.150	.079	.105
Cyclohexane	.139	+	+	.392	1.377	.650	2.100	.048	.139
3-Methylhexane	.076	.513	1.729	.447	+	13.559	.447	.068	.123
Methylcyclohexane	.108	.783	1.868	.579	.835	8.920	.598	.128	.627
2,5-Dimethylhexane	.089	.674	2.319	.544	.689	6.806	.662	.132	.240
2,3,4-Trimethylpentane	.118	1.524	2.293	1.235	1.480	26.090	.882	.122	.181
3-Methylheptane	.223	2.213	2.500	.521	1.739	7.770	1.000	.156	.231
2,2,5-Trimethylhexane	.119	2.907	+	.438	.902	12.104	.802	.161	.163
1,4-Dimethylbenzene	.274	5.773	2.462	1.423	1.448	12.480	2.481	.096	.658

(continued)

TABLE B.13. (continued)

	Plot # 5						
	10/7/82	10/12/82		11/24/82	12/02/82	5/9/83	
	BT	AA	AT,AA	BA	BT	BT	AT
Pentane	+	+	+	.032	.029	+	.044
Cyclopentane	+	+	+	.114	.113	+	.218
Hexane	+	+	+	.044	.034	+	.023
Methylcyclopentane	+	+	+	.316	.277	.145	.570
Benzene	+	2.879	2.345	2.071	1.534	.323	.707
2,4-Dimethylpentane	+	.195	.210	.343	.212	.044	.190
Cyclohexane	.073	+	+	.144	.140	.040	.123
3-Methylhexane	.076	.955	1.041	.187	.128	.034	.134
Methylcyclohexane	.061	.831	1.169	1.118	1.090	.258	.679
2,5-Dimethylhexane	+	.866	1.657	.186	.104	.077	.223
2,3,4-Trimethylpentane	.112	3.486	3.040	.288	.174	.066	.165
3-Methylheptane	.657	11.970	12.597	.309	.131	.094	.425
2,2,5-Trimethylhexane	.183	+	+	.208	.117	+	.181
1,4-Dimethylbenzene	.557	20.770	16.610	.878	.408	.190	.660

(continued)

TABLE B.13. (continued)

	Plot # 7 5/9/83 IAT	 30 min. AT	Plot # 1 6/9/83 AT
Pentane	.004	.065	.044
Cyclopentane	.041	.280	.285
Hexane	.034	.023	.035
Methylcyclopentane	.282	.522	.597
Benzene	.289	.508	.611
2,4-Dimethylpentane	.100	.088	.177
Cyclohexane	.094	.129	.134
3-Methylhexane	.203	.125	.153
Methylcyclohexane	.289	.616	.732
2,5-Dimethylhexane	.073	.110	.197
2,3,4-Trimethylpentane	.193	.211	.310
3-Methylheptane	.110	.110	.343
2,2,5-Trimethylhexane	.075	.065	.238
1,4-Dimethylbenzene	.423	.472	.782

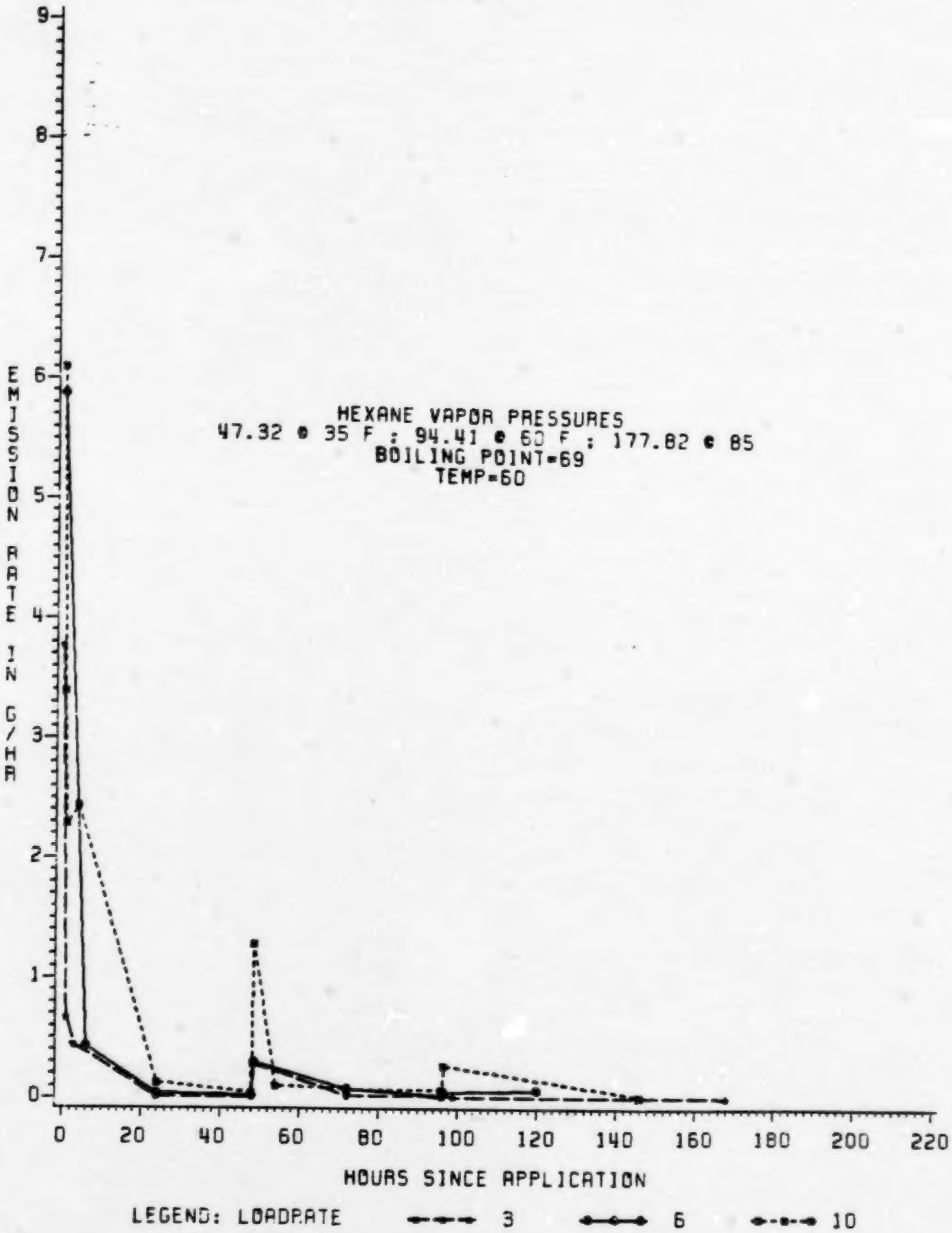

Figure B.1. Time relation of emission rate and loading rate-Hexane.

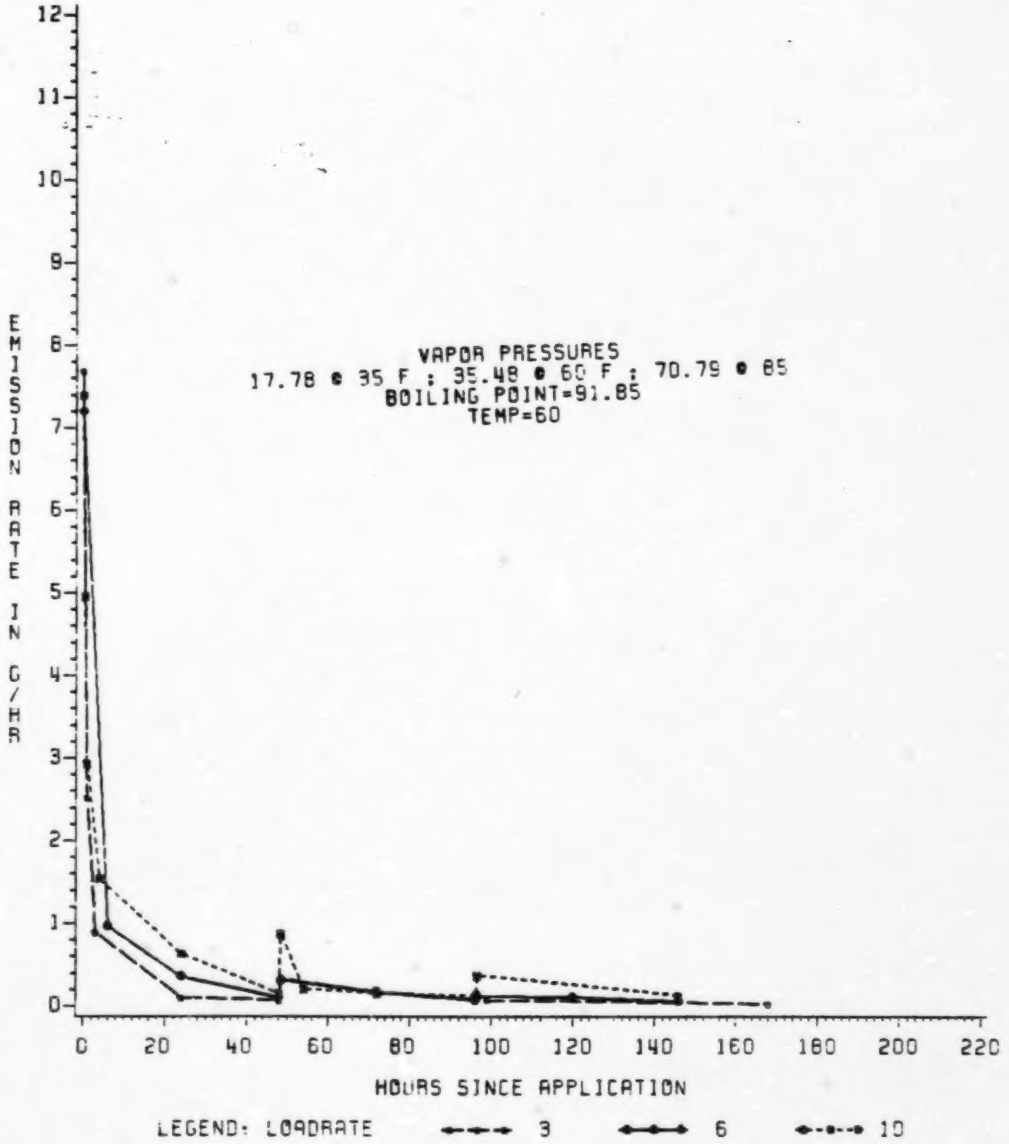

Figure B.2. Time relation of emission rate and loading rate-3-Methylhexane, temp. = 60°F.

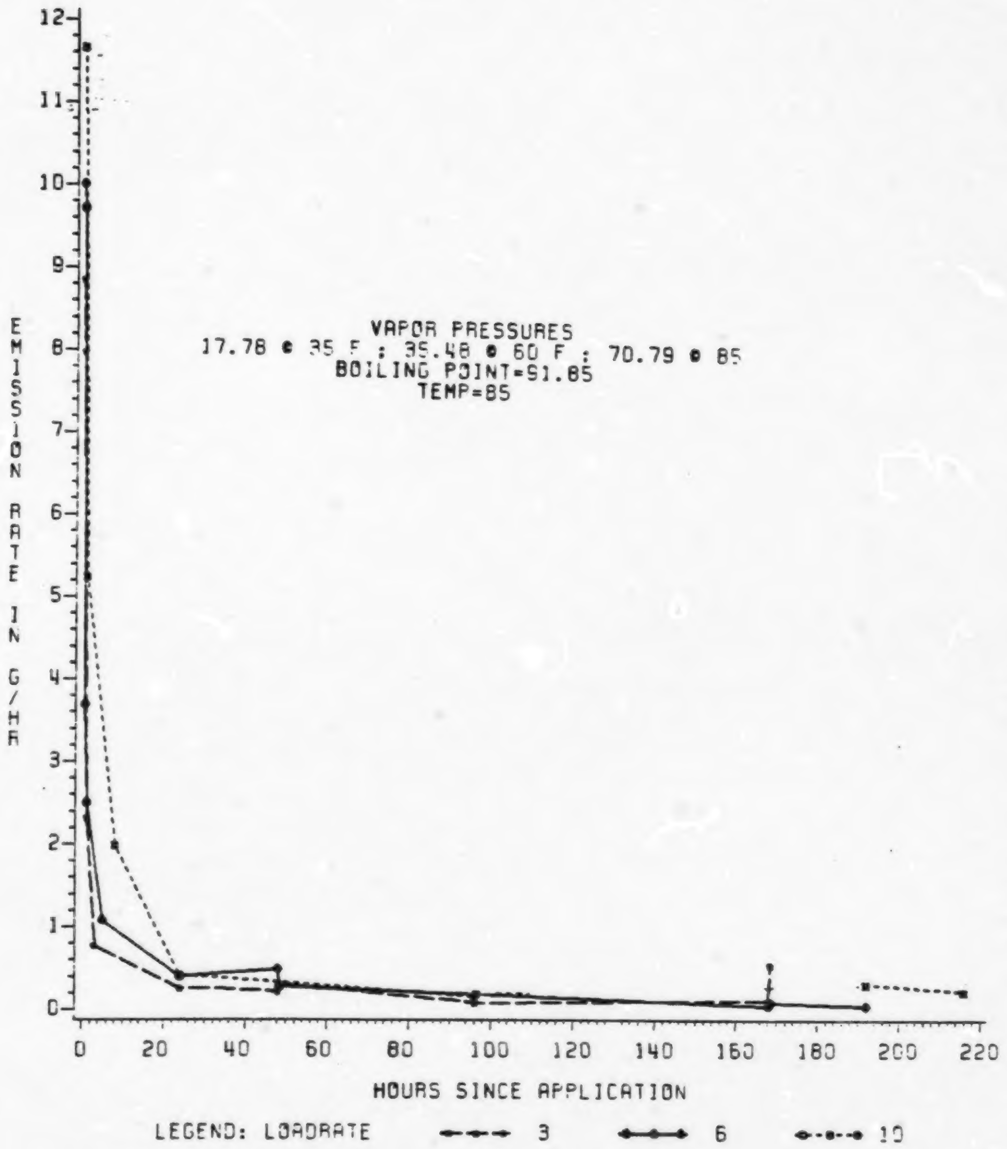

Figure B.3. Time relation of emission rate and loading rate-3-Methylhexane, temp. = 85°F.

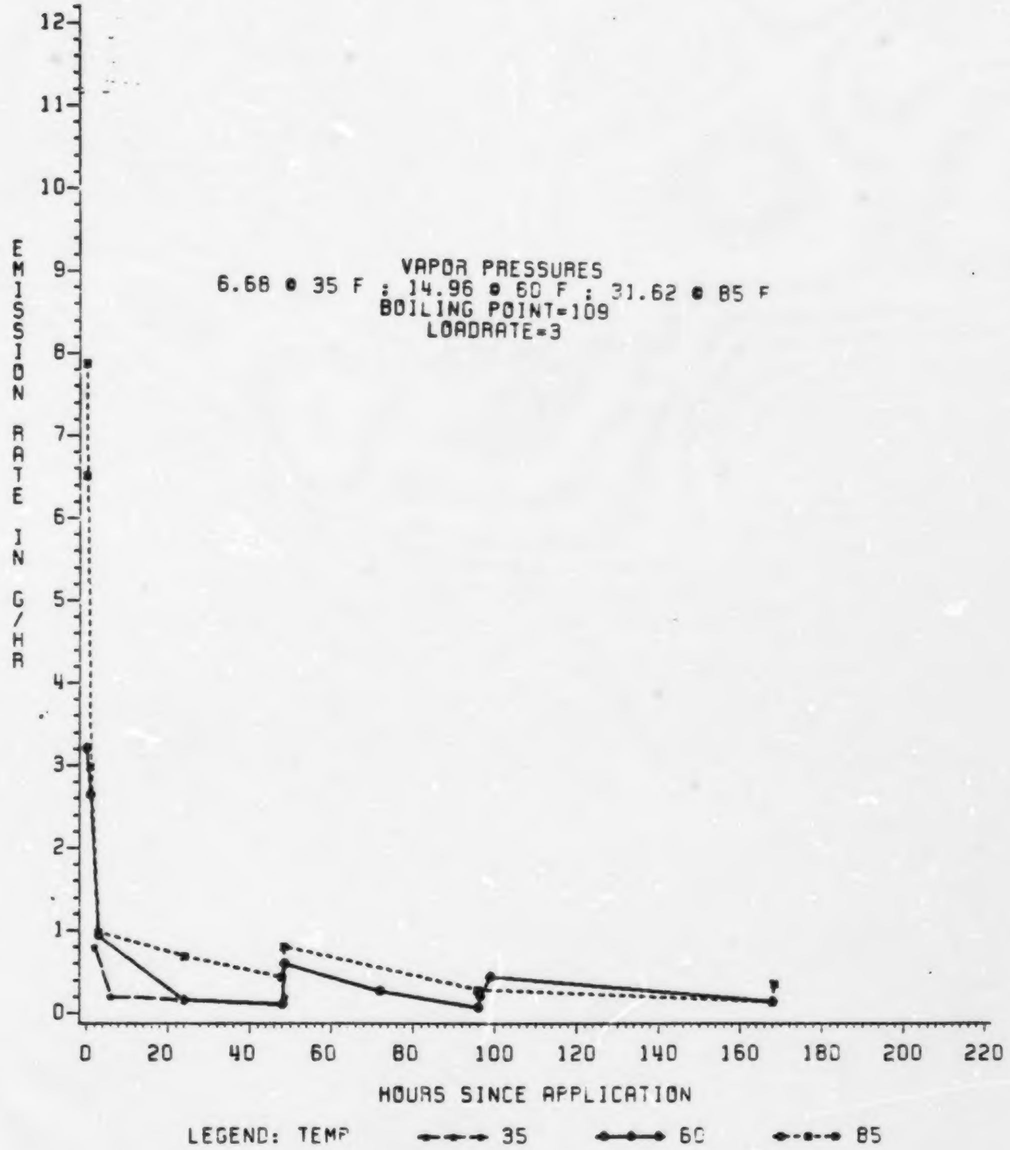

Figure B.4. Time relation of emission rate and temperature-2,5-Dimethylhexane, loading rate = 3.

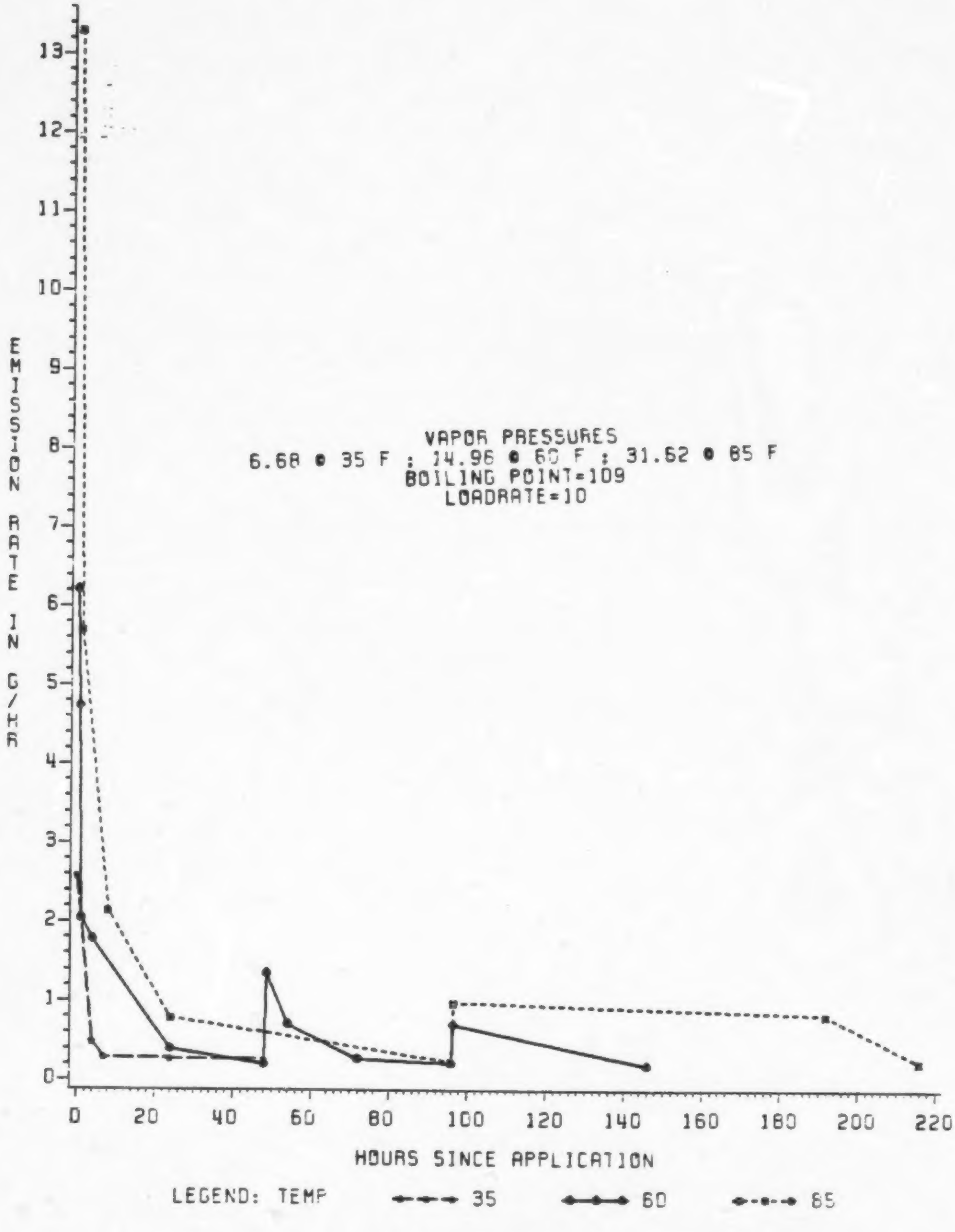

Figure B.5. Time relation of emission rate and temperature-2,5-Dimethylhexane, loading rate = 10.

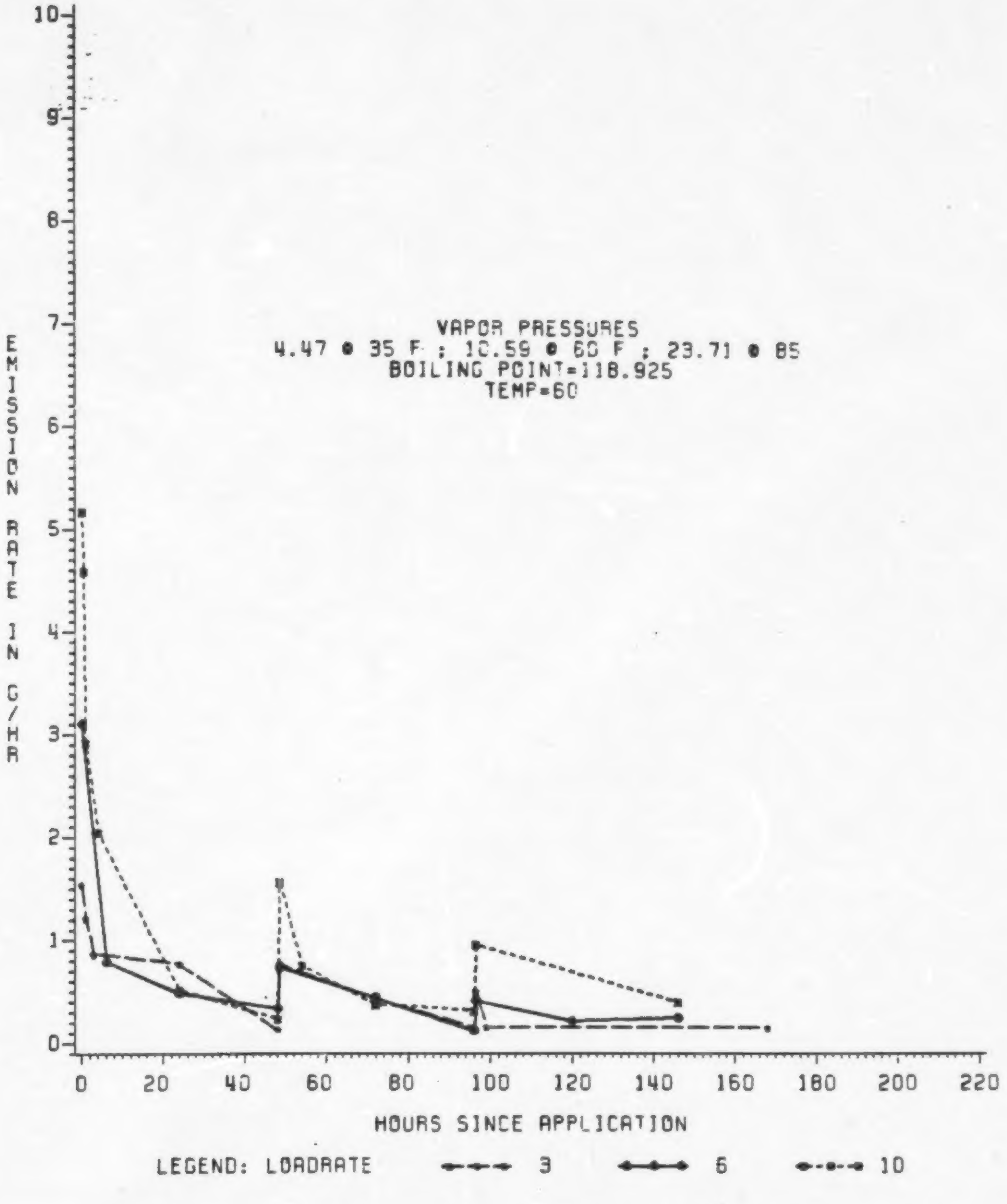

Figure B.6. Time relation of emission rate and loading rate-3-Methylheptane, temp. = 60°F.

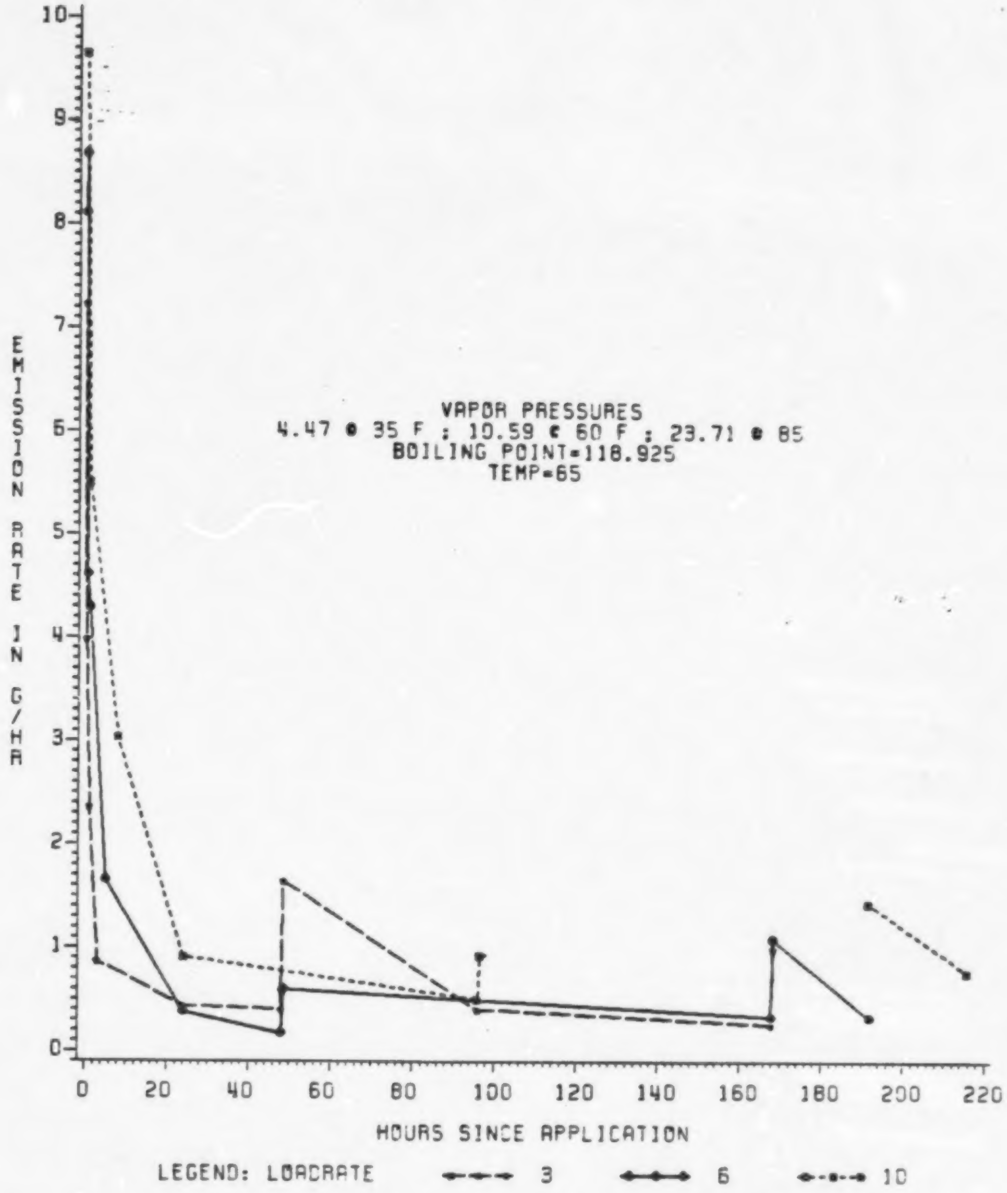

Figure B.7. Time relation of emission rate and loading rate-3-Methylheptane, temp. = 85°F.

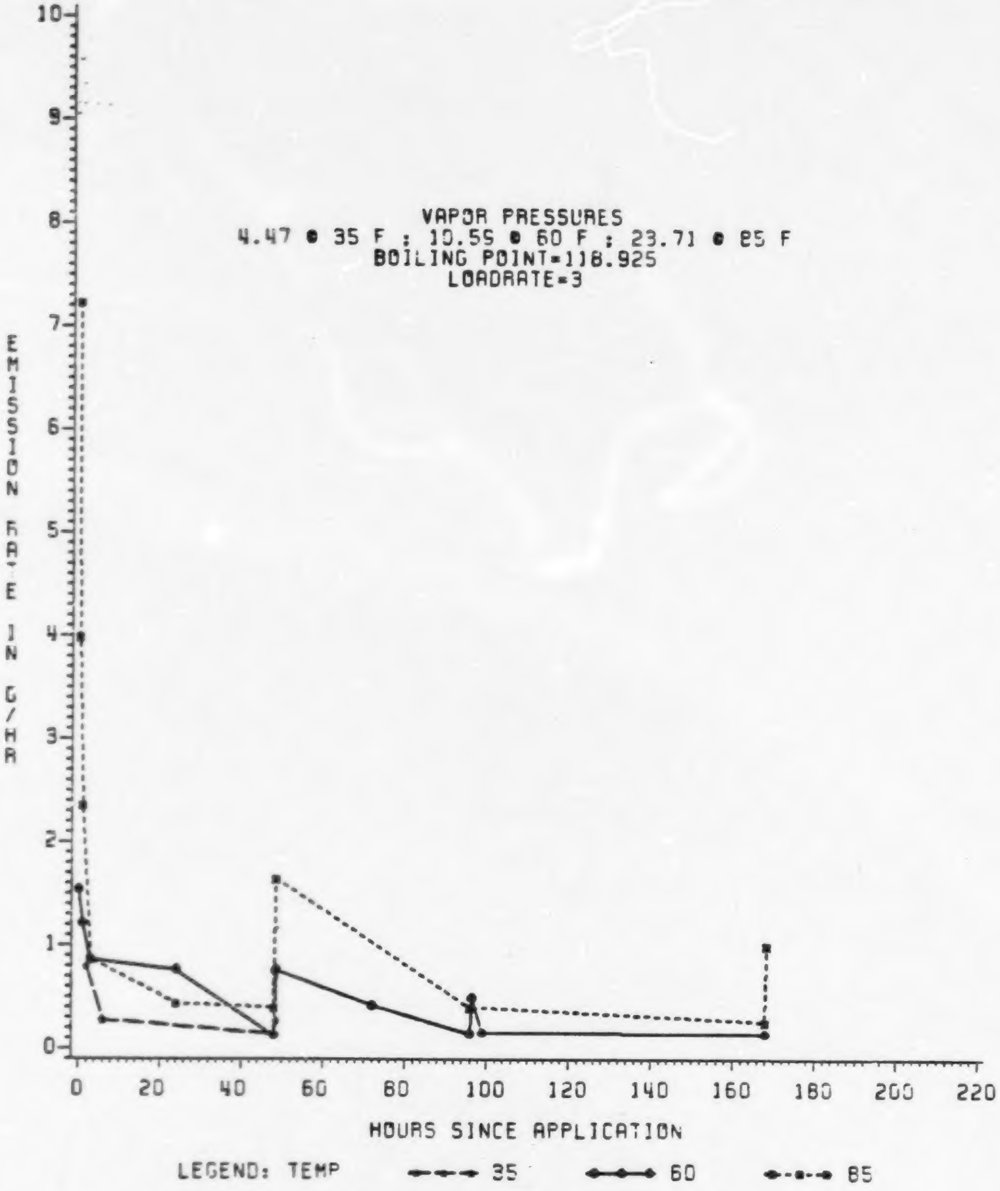

Figure B.8. Time relation of emission rate and temperature-3-Methylheptane, loading rate = 3.

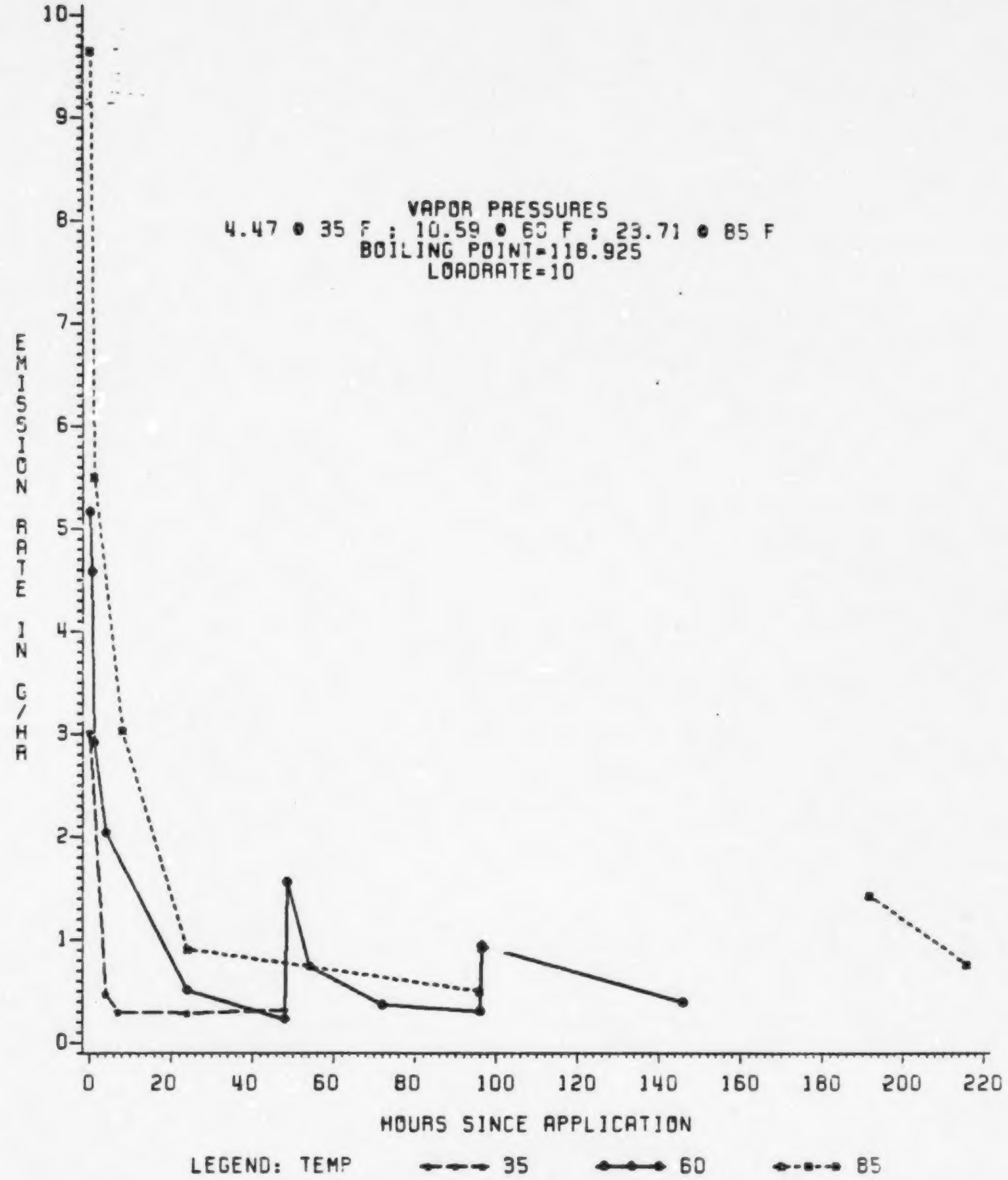

Figure B.9. Time relation of emission rate and temperature-3-Methylheptane, loading rate = 10.

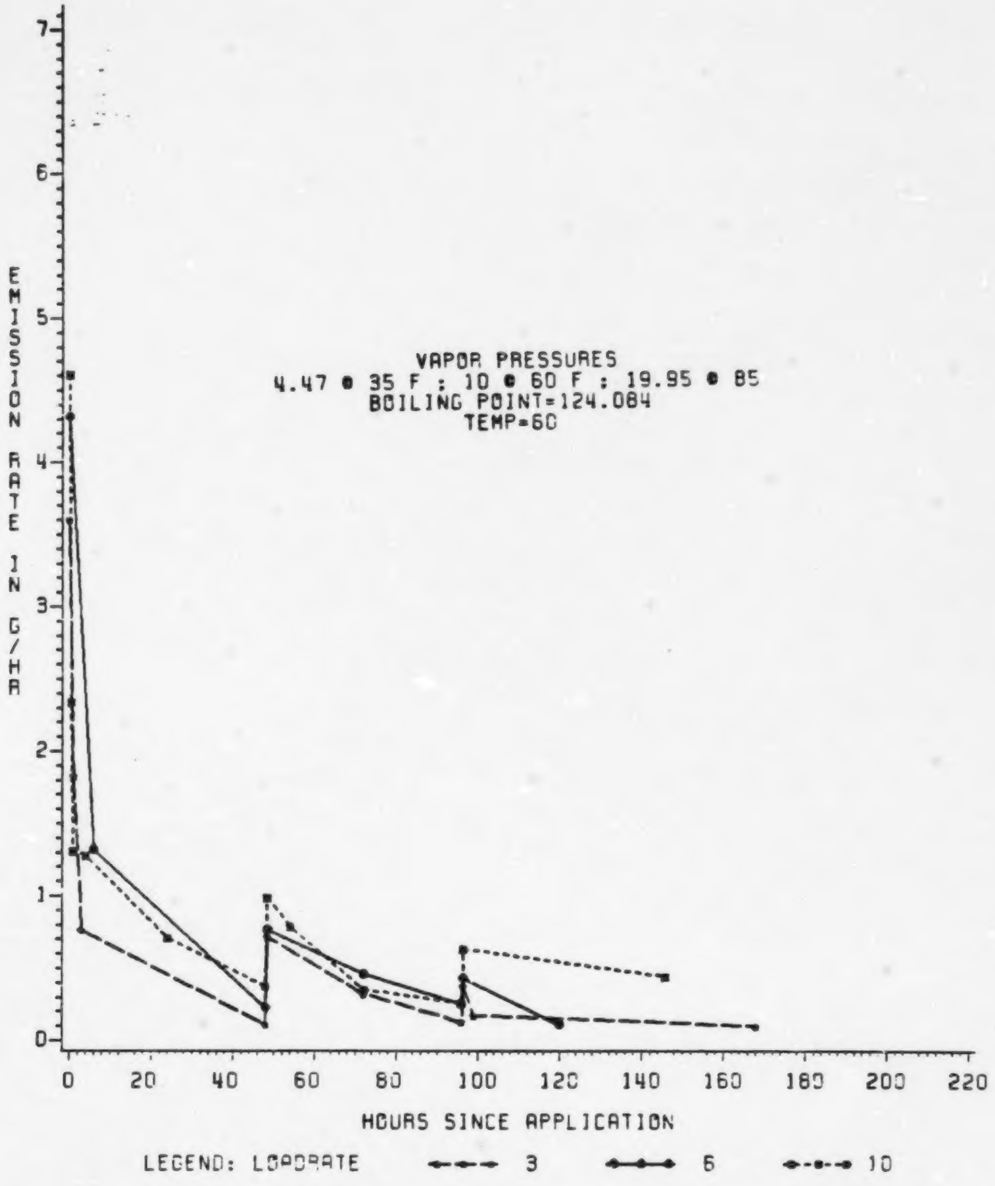

Figure B.10. Time relation of emission rate and loading rate-2,2,5-Trimethylhexane, temp. = 60°F.

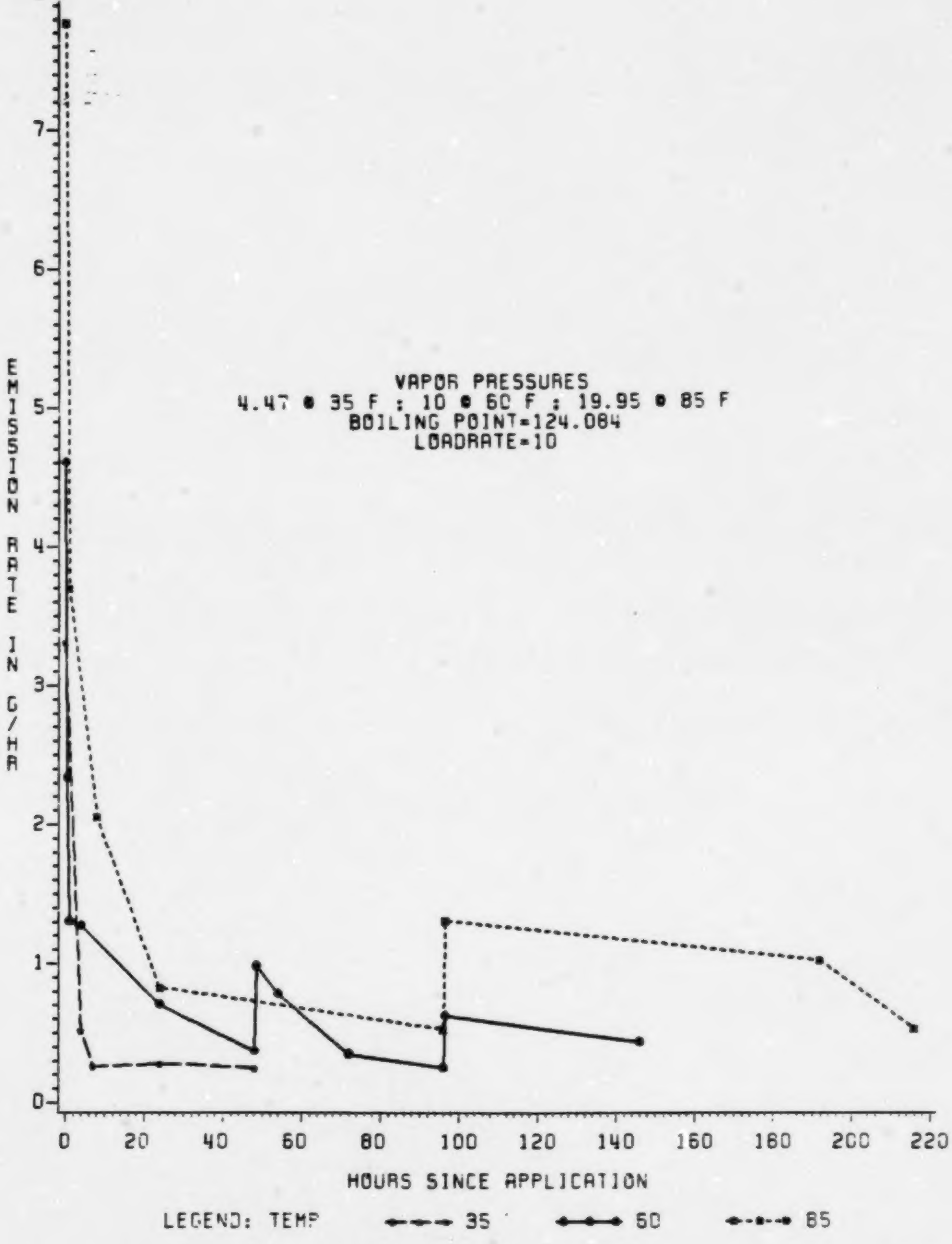

Figure B.11. Time relation of emission rate and temperature-2,2,5-Trimethylhexane loading rate = 10.

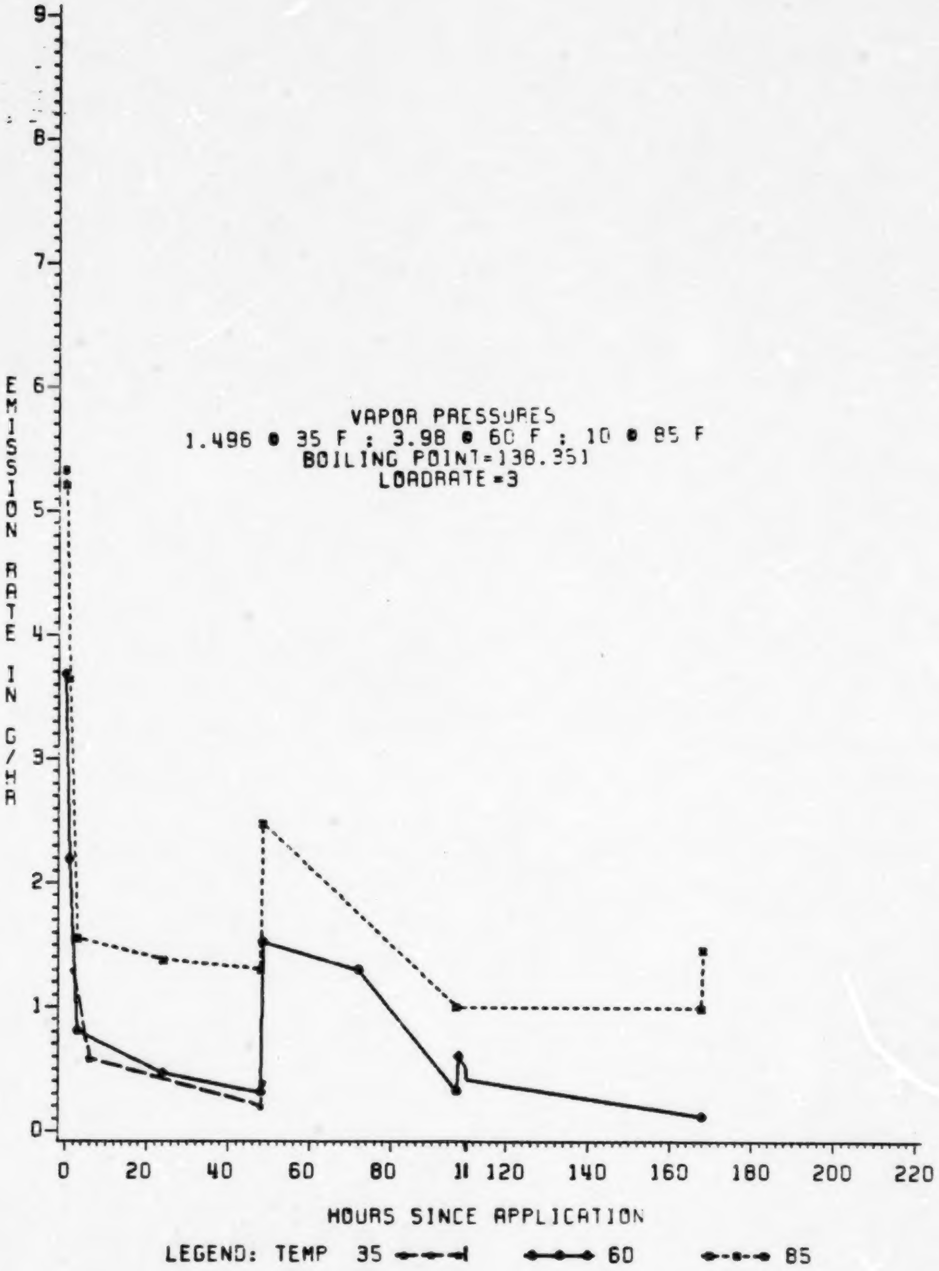

Figure B.12. Time relation of emission rate and temperature-1,4-Dimethylbenzene, loading rate = 3.

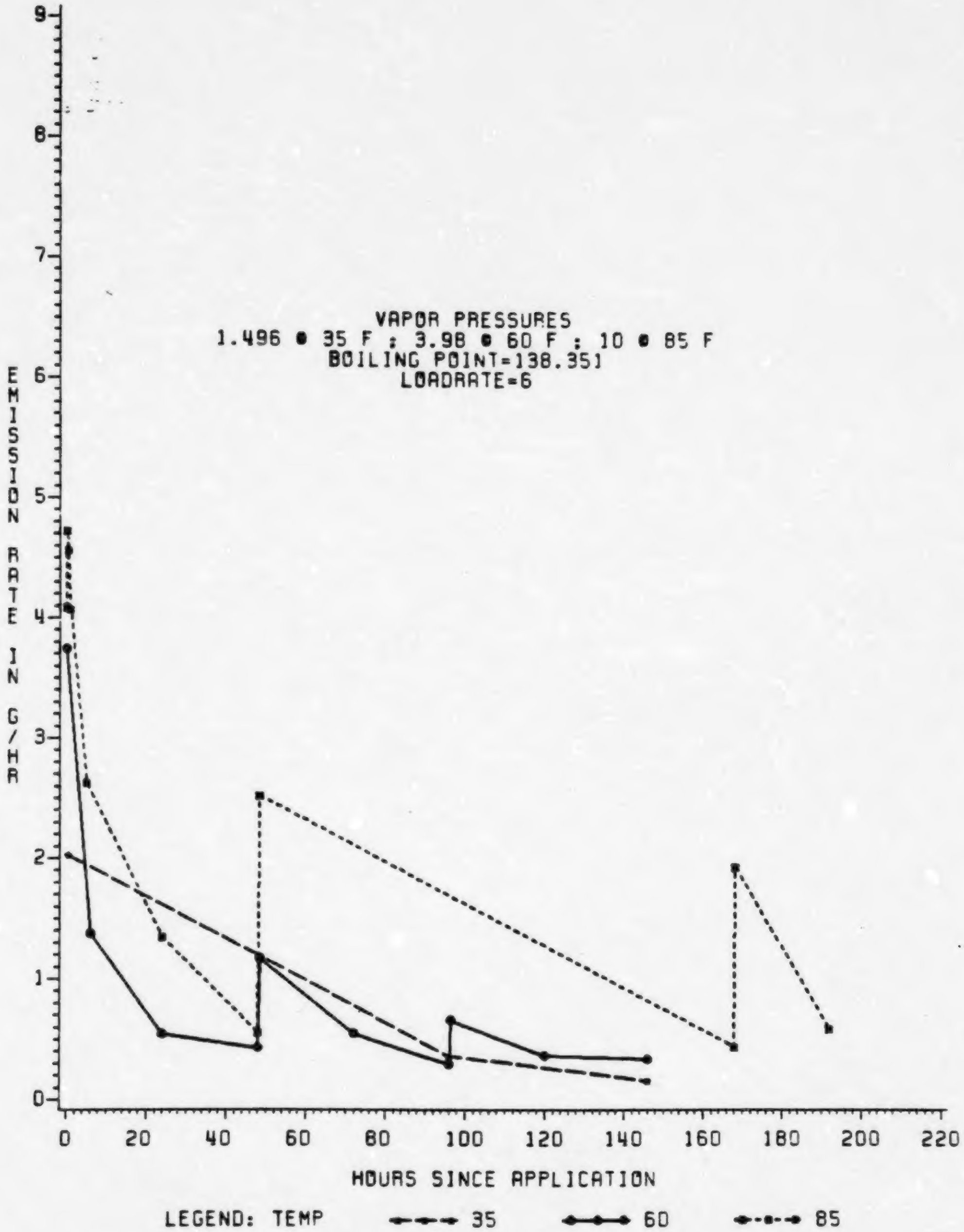

Figure B.13. Time relation of emission rate and temperature-1,4-Dimethylbenzene, loading rate = 6.

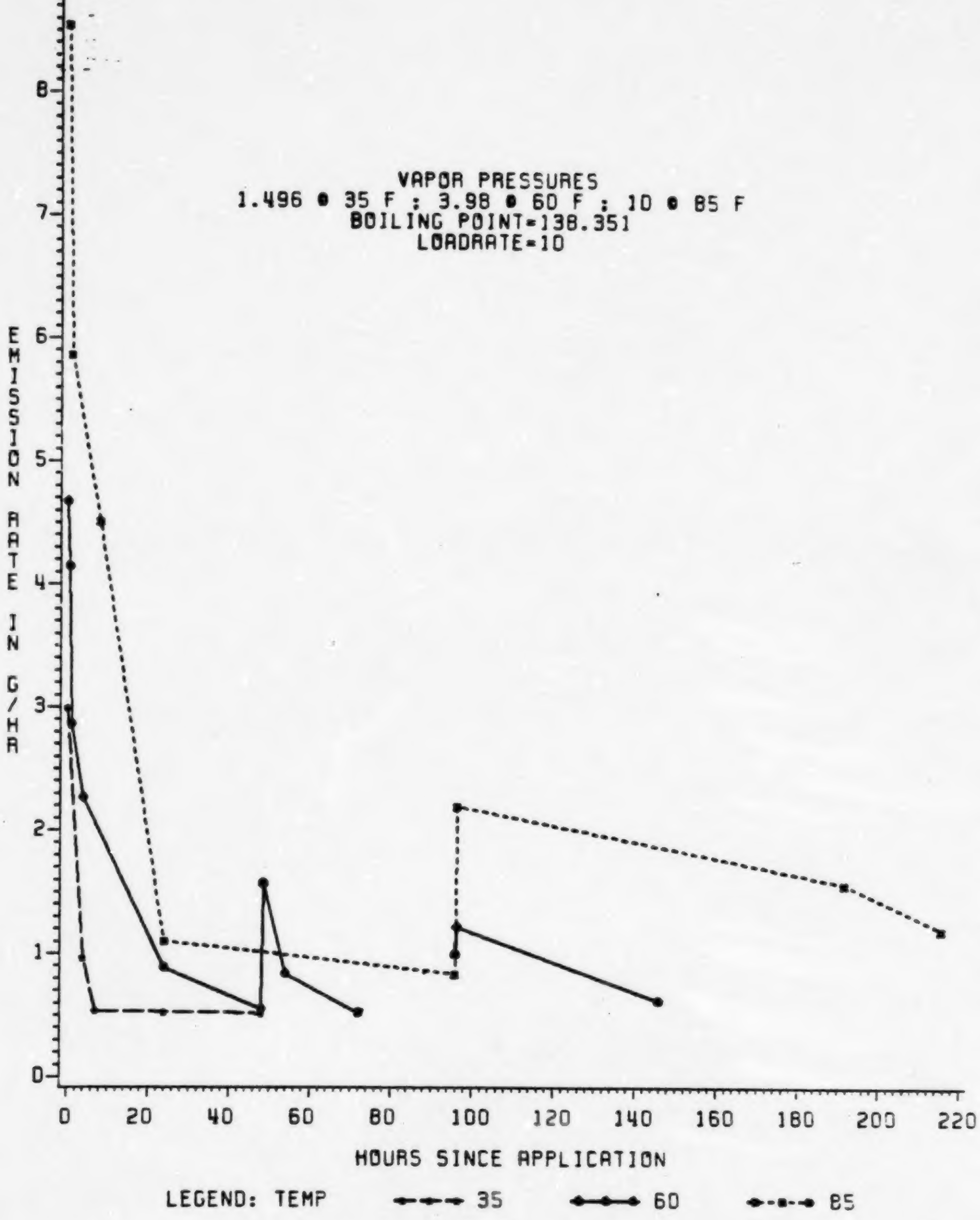

Figure B.14. Time relation of emission rate and temperature-1,4-Dimethylbenzene, loading rate = 10.

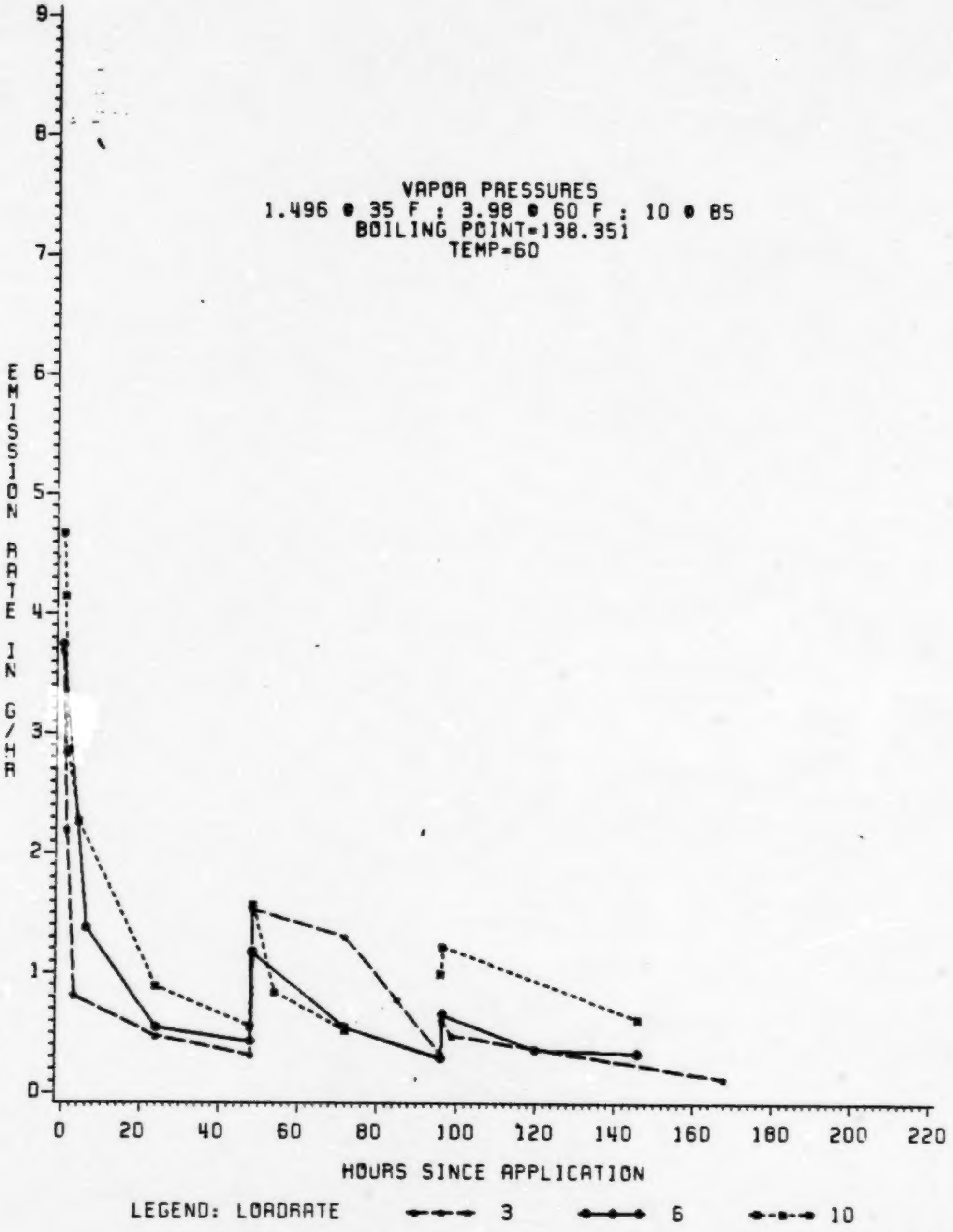

Figure B.15. Time relation of emission rate and loading rate-1,4-Dimethylbenzene, temp. = 60°F.

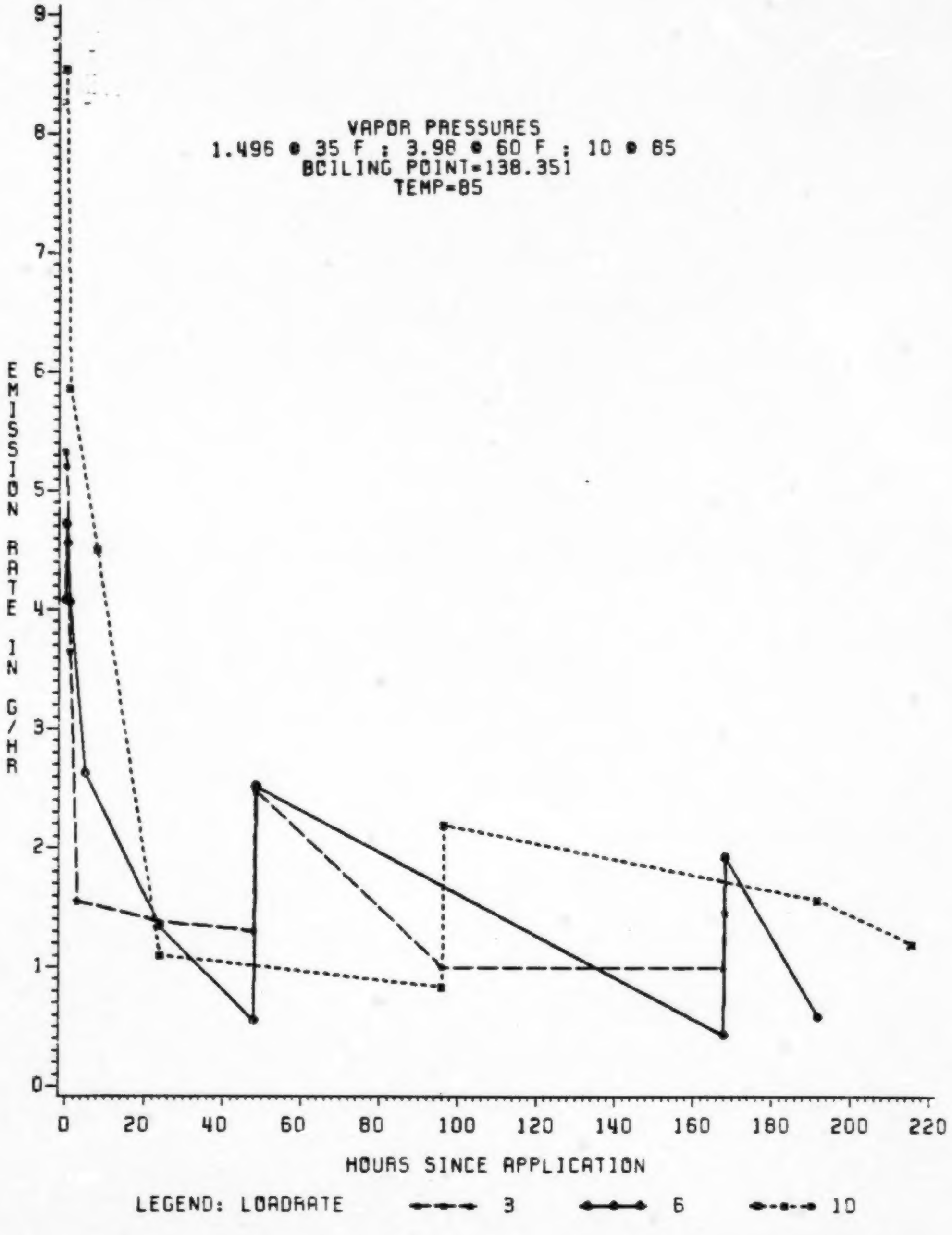

Figure B.16. Time relation of emission rate and loading rate-1,4-Dimethylbenzene, temp = 85°F.

APPENDIX C

HEAVY METAL DATA

TABLE C.1. SOIL METAL DATA
(mg/kg)

Plot	Zn	Ni	Cu	Pb	Cr	Cd	Date
1	37.0	8.0	12.0	15.0	22.0	0.00	111782
2	40.0	32.0	22.0	20.0	94.0	0.00	70682
2	30.0	34.0	16.0	20.0	104.0	0.00	70682
2	36.0	30.0	12.0	20.0	98.0	0.00	92282
2	36.0	22.0	12.0	20.0	66.0	0.00	92282
2	63.0	16.0	140.0	24.0	32.0	0.00	111782
2	.	14.0	110.0	20.0	22.0	0.00	111782
2	56.0	18.0	15.0	18.0	22.0	0.55	122082
3	30.0	22.0	14.0	20.0	92.0	0.00	70682
3	32.0	28.0	16.0	20.0	80.0	0.00	70682
3	30.0	22.0	14.0	20.0	92.0	0.00	70682
3	32.0	28.0	16.0	20.0	80.0	0.00	70682
4	16.0	24.0	8.0	40.0	108.0	0.00	70682
4	14.0	26.0	10.0	40.0	76.0	0.00	70682
4	37.0	14.0	38.5	12.0	23.0	0.00	92282
4	48.0	11.5	98.5	5.5	26.5	0.00	92282
4	29.5	0.0	37.0	16.0	21.5	0.50	92282
4	27.0	11.0	25.0	16.0	11.0	0.00	111782
5	46.0	11.5	66.0	13.0	30.5	0.00	92282
5	45.0	10.5	74.0	14.0	24.5	0.00	92282
5	41.0	19.0	43.0	7.0	30.5	0.00	100782
5	40.0	17.5	31.5	5.5	35.5	0.00	100782
5	38.0	13.5	31.5	8.5	21.5	0.00	100782
5	36.0	17.0	16.0	12.0	24.0	0.00	111782
5	43.0	20.0	30.0	26.0	27.0	0.00	111782
6	40.0	6.0	14.0	30.0	92.0	0.00	30282
6	45.0	20.0	55.0	26.0	31.0	0.00	111782
6	43.0	20.0	25.0	28.0	23.0	0.00	111782
7	38.0	6.0	12.0	20.0	80.0	0.00	30282
7	36.0	40.0	14.0	40.0	112.0	0.00	70682
7	40.0	24.0	14.0	40.0	86.0	0.00	70682
7	26.0	38.0	14.0	20.0	74.0	0.00	92282
7	62.0	28.0	170.0	40.0	102.0	0.00	92282
7	66.5	11.0	176.0	8.0	24.5	0.00	100782
7	66.5	12.0	165.0	4.0	24.5	0.00	100782
7	63.5	9.5	170.0	12.0	24.0	0.00	100782
7	67.0	18.0	.	22.0	26.0	0.00	111782
7	67.0	21.0	.	22.0	20.0	0.00	111782
8	87.0	16.0	10.0	14.0	24.0	2.00	60983
8	79.5	15.0	9.5	14.5	22.5	2.00	60983
8	46.0	36.0	30.0	20.0	70.0	0.00	91082
8	36.0	14.0	32.0	20.0	60.0	0.00	91082
8	77.5	26.5	177.5	5.0	31.5	0.00	92682
8	37.0	20.0	23.0	23.0	26.0	0.00	111782
8	33.0	20.0	24.0	25.0	22.0	0.00	111782

(continued)

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Table C.1. (continued)

Plot	Zn	Ni	Cu	Pb	Cr	Cd	Date
9	12.0	24.0	10.0	.	.	0.00	70682
9	36.0	28.0	12.0	20.0	.	0.00	70682
9	52.0	18.5	111.0	5.0	29.5	0.00	92282
9	35.0	11.0	11.5	13.5	21.5	0.00	92282
9	48.0	6.0	11.1	13.5	26.0	0.00	92282
9	31.0	2.5	11.5	13.5	26.5	0.50	92282
9	47.5	13.5	75.0	14.0	24.5	0.00	100782
9	28.0	18.0	20.0	14.0	12.0	0.00	111782
9	33.0	15.0	21.0	16.0	19.0	0.00	111782
10	41.5	21.5	11.5	14.0	29.0	0.00	60983
10	40.0	12.5	9.0	11.0	25.5	0.00	60983
10	36.5	12.5	9.0	21.0	20.0	0.00	60983
10	38.0	18.0	10.0	20.0	.	0.00	70682
10	84.0	28.0	8.0	40.0	.	0.00	70682
10	29.0	11.5	20.5	14.0	30.0	0.00	91082
10	45.0	15.0	25.0	18.0	14.0	0.00	110982
11	39.0	16.0	54.0	14.0	22.0	0.00	111782
11	34.0	11.0	24.0	22.0	18.0	0.00	111782
12	30.0	28.0	8.0	40.0	84.0	0.00	70682
12	24.0	28.0	8.0	40.0	78.0	0.00	70682
13	36.0	24.0	14.0	20.0	92.0	0.00	30282
13	47.5	12.0	10.0	13.5	25.5	0.50	60983
13	50.0	11.5	9.5	18.5	25.5	1.50	60983
13	51.0	12.5	10.0	18.5	28.5	1.00	60983
13	44.5	13.0	11.0	17.5	27.0	1.00	60983
13	18.0	14.0	4.0	20.0	90.0	0.00	70682
13	14.0	16.0	8.0	0.0	96.0	0.00	70682
13	58.0	32.0	180.0	20.0	76.0	0.00	92282
13	54.0	30.0	50.0	20.0	86.0	0.00	92282
13	30.0	90.0	10.0	20.0	88.0	0.00	92282
13	59.0	11.0	130.0	7.0	22.0	0.50	100782
13	65.0	10.5	149.5	13.5	30.0	0.00	100782
13	31.0	16.0	24.0	12.0	12.0	0.00	111782
13	35.0	12.0	18.0	12.0	19.0	0.00	111782
13	35.0	21.0	24.0	24.0	22.0	0.00	111782
13	53.0	17.0	23.0	18.0	24.0	0.25	122082
13	53.0	13.0	13.0	16.0	20.0	0.55	122082
14	14.0	34.0	8.0	40.0	.	0.00	70682
14	20.0	32.0	4.0	20.0	.	0.00	70682
14	14.0	0.0	4.0	20.0	106.0	0.00	70682
14	37.0	12.5	92.0	12.0	18.5	0.00	92282
14	52.5	14.5	112.0	1.5	28.5	0.00	92282
14	61.0	13.5	154.0	16.5	25.5	0.00	100782
15	36.0	16.0	8.5	12.5	18.5	0.00	60983
15	20.0	36.0	6.0	20.0	82.0	0.00	70682
15	16.0	32.0	8.0	40.0	80.0	0.00	70682
15	24.0	10.5	19.0	0.0	21.5	0.00	91082
15	27.0	12.0	24.0	20.0	33.0	0.00	91082
15	58.0	28.5	141.5	5.0	24.5	0.00	92682
15	68.5	18.0	193.0	15.0	24.5	0.00	92682
15	40.0	16.0	34.0	18.0	16.0	0.00	110982

(continued)

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Table C.1. (continued)

Plot	Zn	Ni	Cu	Pb	Cr	Cd	Date
16	67.0	18.0	182.5	13.5	21.0	0.00	92682
16	41.0	14.0	81.0	16.0	18.0	0.00	111782
16	40.0	15.0	79.0	14.0	13.0	0.00	111782
16	44.0	16.0	.	16.0	16.0	0.00	111782
16	27.0	12.0	22.0	16.0	14.0	0.00	111782
17	83.5	18.5	218.0	17.0	32.5	0.00	92682
17	38.0	14.0	51.0	14.0	18.0	0.00	111782
18	43.0	16.0	9.0	11.5	25.5	0.00	60983
18	32.0	26.0	10.0	20.0	90.0	0.00	70682
18	32.0	24.0	14.0	20.0	90.0	0.00	70682
18	30.0	28.0	12.0	20.0	90.0	0.00	92282
18	38.0	48.0	28.0	40.0	88.0	0.00	92282
18	32.0	22.0	10.0	20.0	96.0	0.00	92282
18	28.0	32.0	12.0	20.0	82.0	0.00	92282
18	18.0	28.0	8.0	20.0	82.0	0.00	92282
18	35.0	35.0	18.0	16.0	22.0	0.00	111782
19	18.0	36.0	10.0	20.0	92.0	0.0	70682
19	12.0	32.0	8.0	40.0	.	0.0	70682
20	32.0	0.0	12.0	20.0	68.0	0.0	30282
20	46.5	25.5	11.5	10.5	29.5	0.5	60983
20	45.5	19.0	11.0	12.0	28.5	0.0	60983
20	48.0	10.5	11.0	17.0	24.5	1.0	60983
20	45.0	11.5	16.5	13.0	21.5	0.0	60983
20	43.5	12.0	19.5	11.0	24.0	0.5	60983
20	34.0	34.0	14.0	40.0	.	0.0	70682
20	26.0	26.0	6.0	20.0	.	0.0	70682
20	14.0	26.0	12.0	20.0	104.0	0.0	70682
20	36.5	7.0	65.5	12.0	23.0	0.0	92282
20	39.0	7.0	64.5	7.5	22.0	0.0	92282
20	44.5	11.5	70.5	14.5	22.5	0.0	92282
20	47.5	11.5	57.0	13.0	23.5	0.0	92282
20	39.0	13.0	71.0	10.5	20.5	0.0	92382
20	38.0	14.0	66.0	14.0	14.0	0.0	111782
20	45.0	17.0	96.0	16.0	16.0	0.0	111782
20	33.0	16.0	15.0	18.0	17.0	0.0	111782
21	66.0	10.5	9.5	15.5	20.0	1.5	60983
21	61.5	11.0	9.5	14.0	27.5	2.0	60983
21	79.5	13.0	10.0	20.5	29.5	2.0	60983
21	30.0	34.0	22.0	20.0	84.0	0.0	91082
21	.	14.0	174.0	18.0	20.0	0.0	110982
21	33.0	11.0	47.0	16.0	12.0	0.0	111782
22	72.0	12.5	9.5	20.0	27.0	2.5	60983
22	90.0	13.0	9.0	17.5	27.5	2.0	60983
22	24.0	24.0	12.0	30.0	98.0	0.0	92282
22	42.0	19.0	28.0	23.0	26.0	0.0	111782
22	45.0	20.0	57.0	20.0	29.0	0.0	111782
23	64.0	20.5	120.0	14.0	27.5	0.0	92282
23	139.0	18.0	80.0	18.0	16.0	0.0	110982
23	47.0	21.0	80.0	17.0	16.0	0.0	110982
24	22.0	32.0	10.0	60.0	.	0.0	70682
24	22.0	38.0	6.0	20.0	.	0.0	70682
24	30.0	20.0	10.0	20.0	.	0.0	70682
24	26.0	12.0	24.5	2.0	22.5	0.0	91082
24	132.0	15.0	94.0	32.0	14.0	0.0	110982
24	53.0	17.0	140.0	29.0	23.0	0.0	111782
24	47.0	19.0	95.0	26.0	22.0	0.0	111782

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Table C.1. (continued)

Plot	Zn	Ni	Cu	Pb	Cr	Cd	Date
25	26.0	30.0	12.0	20.0	62.0	0.0	30282
25	28.0	32.0	10.0	20.0	88.0	0.0	70682
25	20.0	22.0	12.0	20.0	98.0	0.0	70682
25	30.0	36.0	20.0	40.0	76.0	0.0	91082
25	28.0	38.0	18.0	30.0	106.0	0.0	91082
25	15.0	9.5	151.0	3.0	23.0	0.5	91082
25	67.0	15.0	174.5	19.0	26.5	0.0	92282
25	71.0	5.5	181.0	14.0	29.0	0.5	92282
25	60.5	5.0	142.5	15.5	26.0	0.0	92282
25	65.0	3.0	170.0	12.0	22.0	0.5	92282
25	34.0	15.0	40.0	15.0	14.0	0.0	111782
25	53.0	17.0	75.0	18.0	26.0	0.0	111782
26	28.0	32.0	.	20.0	52.0	0.0	30282
26	49.0	17.0	9.0	15.0	21.5	0.5	60983
26	51.5	18.0	10.0	12.5	25.0	0.5	60983
26	48.5	19.0	10.0	11.5	24.5	0.5	60983
26	38.0	14.0	52.0	16.0	24.0	0.00	111782
26	36.0	15.0	49.0	12.0	20.0	0.00	111782
26	184.0	14.0	22.0	20.0	18.0	1.85	122082
26	153.0	19.0	23.0	18.0	18.0	0.75	122082
27	30.0	26.0	18.0	40.0	94.0	0.00	70682
27	36.0	34.0	16.0	20.0	112.0	0.00	70682
28	43.0	18.0	10.0	13.0	25.5	0.00	60983
28	45.5	17.5	10.5	12.5	29.0	0.00	60983
28	.	10.0	8.0	0.0	92.0	0.00	70682
28	57.5	9.5	143.0	0.0	21.5	0.50	92282
28	122.0	18.0	23.0	21.0	20.0	0.00	110982
28	46.0	19.0	19.0	16.0	14.0	0.00	110982
29	36.0	32.0	8.0	20.0	.	0.00	70682
29	14.0	20.0	8.0	40.0	.	0.00	70682
29	29.5	13.0	33.0	7.0	18.5	0.00	92682
29	74.5	11.5	136.5	19.0	25.0	0.00	92682
29	29.5	11.5	30.0	0.0	17.5	1.00	110982
30	18.0	34.0	12.0	20.0	84.0	0.00	70682
30	20.0	26.0	10.0	40.0	.	0.00	70682
30	92.5	14.5	297.0	7.5	27.0	0.00	92682
30	94.0	14.5	288.0	14.5	20.5	0.00	92682
30	32.0	13.0	20.0	22.0	14.0	0.00	111782
30	29.0	14.0	24.0	17.0	16.0	0.00	111782
31	39.0	25.0	25.5	13.5	30.0	0.00	92682
31	29.0	10.0	33.0	20.0	16.0	0.00	111782
31	33.0	15.0	37.0	15.0	20.0	0.00	111782

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TABLE C.2. BACKGROUND SOILS METALS

SAMPLE	CU	CR	PB	ZN	NI	CD
1	26.9	47.6	14.2	.	65.1	0.8
2	7.5	11.8	15.0	35.2	21.3	0.5
3	69.6	5.8	19.0	77.5	16.7	0.2
4	7.5	14.3	13.0	26.1	25.3	0.9
5	15.4	19.1	27.0	.	21.4	1.4
6	8.6	15.6	12.9	35.9	33.0	0.6
7	6.1	6.8	8.9	29.1	20.6	1.2
8	6.4	7.6	4.9	19.8	15.9	0.2
9	6.1	8.5	13.9	19.1	15.6	0.5
10	6.6	11.3	12.9	19.0	14.4	0.0
11	19.1	16.9	20.8	42.8	27.2	0.2
12	20.8	29.2	12.0	42.4	43.1	0.1
13	24.0	8.7	18.0	36.2	15.3	2.5
14	12.1	12.4	14.0	34.6	31.0	0.0
15	6.5	12.8	18.0	30.3	22.1	0.0
16	6.3	10.4	18.0	24.1	21.7	0.0
17	3.0	14.3	16.0	34.1	3.9	0.2
18	6.1	11.4	14.0	21.2	31.5	0.0
19	5.6	9.7	6.9	19.0	9.5	0.0
20	5.2	8.2	17.8	24.6	13.2	0.0
21	5.9	8.5	16.0	21.6	16.9	0.0
22	1.1	8.1	12.0	31.0	30.1	0.3
23	6.6	9.8	17.7	89.1	14.3	0.0
24	8.2	11.3	17.8	41.2	13.6	0.0
25	15.2	22.1	9.4	54.2	30.8	0.0

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TABLE C.3. SLUDGE ANALYSIS BY BATCH

			mg/kg)			
Batch	Zn	Ni	Cu	Pb	Cr	Cd
1	12.97	22.20	1.00	2.00	0.00	0.25
2	25.49	12.57	0.47	1.12	1.65	0.00
3	812.20	22.62	19.37	50.26	-	-
3	293.34	12.54	8.46	20.84	20.21	13.48
3	500.39	12.71	9.71	22.46	25.42	23.30
3	392.92	10.28	7.01	19.62	24.29	16.35
3	344.29	5.71	2.86	37.14	27.14	14.29
3	216.17	11.16	5.41	11.50	23.05	20.04
3	70.65	8.09	1.80	5.10	16.67	10.65
4	101.94	8.39	5.81	4.84	7.74	1.29
4	177.34	7.72	8.57	11.29	14.29	7.43
4	145.89	6.36	7.73	12.27	12.27	8.18
4	258.99	5.06	6.74	18.54	12.92	8.99
4	319.64	21.04	1.80	5.10	23.05	20.04
4	258.82	14.82	9.26	12.96	10.65	16.67